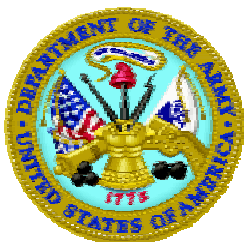# Elimination of Toxic Materials and Solvents from Solid Propellant Components

Sponsored by:

Strategic Environmental Research and Development Program

Final Report

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Table of Contents

Elimination of Toxic Materials and Solvents
from Solid Propellant Compositions

PP-1058

<u>Introduction</u>

The purpose of this report is to document the objective, technical approach and accomplishments of the subject project, commonly referred to as the Green Missile Program.

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<u>Project Background</u>

Solid propellants found in DoD missile systems contain ingredients that are considered hazardous. Specifically, lead is utilized as a ballistic catalyst in minimum smoke systems. Exhaust products are also hazardous. The lead used in minimum smoke propellants is also contained in the missile exhaust products. Additionally, composite propellants contain ammonium perchlorate (AP), which upon combustion produces HCl which is a toxic substance. Chloride ions coming off the HCL molecule in the upper atmosphere can react with and destroy ozone. Lastly, regulated and hazardous solvents are usually

used to process propellants. This poses both a health risk and emission/disposal problems. Alternatives to both lead and AP are required to ensure solid rocket motor propellants are less hazardous during propellant processing and combustion, and solventless processing techniques are required to minimize associated health hazards and emissions.

<u>Objective</u>

The overall goal of the "Green Missile" program is the elimination of major sources of toxic/hazardous materials used in solid rocket propulsion systems. The specific tasks and performers addressing this objective are as follows:

Task	US Army AMCOM	NSWC, IH	NAWC, CL	AFRL	CHPPM	EPA
Develop Lead-free Castable Propellant for Minimum Smoke Systems	X		X			
Develop Lead-free Extrudable Propellant for Minimum Smoke Systems		X				
Develop Complete and Clean, HCl-free, Combustion of Propellant			X	X		X
Develop Solventless Methods for Processing Energetic Oxidizers	X					
Develop Thermoplastic Elastomer Based Inhibitors		X		X		
Perform Toxicology Risk Assessment	X				X	

The remainder of this report is divided into major sections corresponding to each performer on the project. Each section will address technical approach, results, conclusions, summary, transition plan and recommendations. Work done by supporting performers is covered under the corresponding major performer section.

U.S. Army Aviation and Missile Command

Develop Lead Free Castable Propellant for Minimum Smoke Systems

Perform Toxicology Risk Assessment (CHPPM support)

Technical Approach

The approach for Army minimum smoke formulations was to develop alternative propellants that do not contain lead as a ballistic modifier. Two methods were investigated. One approach substituted bismuth compounds for lead compounds in a newly reformulated propellant. The other approach addressed elimination of lead by employing a newly reformulated propellant using Ammonium Dinitramide (ADN) as an oxidizer.   The ADN formulation does not require a ballistic modifier to meet performance requirements.

CHPPM performed some work with regards to a toxicological risk assessment for new ingredients found in the castable lead free formulation.   The approach was to review toxicity data for both the organometallic components and the organic compounds. The changes in formulation of the organometallic components involved replacement of organo-lead compounds and lead oxide with similar compounds such as bismuth. In general, toxicity data was available for the metal compounds or for closely related compounds that could serve as surrogates for the assessment of toxicity. CHPPM has high confidence in the reliability of these comparisons.

Assessment of the toxicity of the organic compounds proposed as replacements for the currently used energetic compounds proved to be more difficult. These compounds were novel in molecular structure, have not been the subject of conventional toxicological studies, and closely related surrogates were not available. As a result of the lack of experimental data, the toxicity assessments of the organic compounds were generally performed by qualitative structure activity relationship (QSAR). The QSAR method relies on assessment of the toxicity of a compound by examination of the functional parts of the molecule that may contribute to overall toxicity.   Although, the method can produce an assessment from only the molecular structure of the compound, the reliability of these predictions improve if structurally related compounds are in the QSAR database.

CHPPM also had planned to evaluate the bismuth formulation exhaust products and their impact on the environment. However, later in the study they determined they could not perform that assessment and informed AMCOM no further effort regarding that task would be expended. To supplement the CHPPM effort, AMCOM performed a literature search regarding the toxicity of bismuth compounds to human health and its effects on the environment.

Accomplishments and Results

Lead-free castable propellant formulations were developed that meet the requirements for use in next generation tactical missiles. Two bismuth compounds were incorporated into high performance propellant formulations and were evaluated for processing, ballistic, mechanical, signature and aging properties. Acceptable test results were achieved in all the aforementioned evaluations. Propellant performance properties were at least equal to current formulations containing lead compounds and were superior to current state of the art (SOTA) formulations in some very important properties (reference Figure 1). The most difficult hurdle to overcome had been ballistic control without lead. Both bismuth salicylate and bismuth citrate exhibited ballistic properties equal in propellant burning rate, burning rate pressure exponent and temperature sensitivity. Bismuth propellant processing required some minor changes in the processing procedure, but these were successfully worked out where propellant potlife values greater than

ten hours have been recorded. Two of these lead-free propellants have been successfully tested in the TOW missile and 2.75 Rocket configurations. Exhaust products yield no lead compounds from the metallic portion of the ballistic catalyst and carbon monoxide, carbon dioxide and water at about the same level as the lead-containing propellants, from the organic portion of the catalyst (reference Figure 2). Thus, much less harmful bismuth products have replaced the lead exhaust products.

Catalyst	New Castable	SOTA 1	SOTA 2
	bismuth salicylate	lead citrate	lead oxide
Burn rate	**0.46**	**0.35**	**0.35**
Burn rate/ pressure relationship	**0.3**	**0.3**	**0.45**
DENSITY (lb/in^3)	**0.0609**	**0.062**	**0.0614**
Thrust (lb-sec/lb)	**248**	**246**	**246**
Thrust density relationship	**15.1**	**15.3**	**15.1**

`Figure 1   Comparison of Green Missile Bismuth Formulation Mechanical Properties to State of the Art Minimum Smoke Formulations

Exhaust Product	SOTA	Lead Free
Al2O3	**0.99**	**0**
CO	33.38	33.94
CO2	22.01	21.66
Pb	**1.27**	**0**
Bismuth Oxide	**0**	**0.05**
Bismuth (liq)	**0**	**1.44**
H2	1.84	1.85
H2O	11.01	10.88
N2	29.42	28.37
Zirconium Oxide	**0**	**1.81**

Figure 2   Results of Thermodynamic Calculations of Bismuth and State of the Art Minimum Smoke Formulation Exhaust Products

Ammonium dinitramide, ADN, is a new solid rocket propellant ingredient that has the potential for dramatically improving rocket performance. It has also been evaluated as an alternative under the Green Missile Program. The ADN contains a ratio of nitrogen, hydrogen, and oxygen atoms which yield exhaust products that are environmentally benign. Through leveraging with three subsequent AMC D650 programs, Propulsion and Structures Directorate has purchased and completed an initial evaluation of ADN in propellant formulations. Through these initial findings, it was determined that ADN is compatible with a number of routinely used solid rocket propellant ingredients. Theoretical performance improvements have also been verified (reference Figure 3). Thermodynamic calculations with ADN in

these formulations show it to yield exhaust products that are environmentally non-hazardous. Natural degradation of the raw material yields ammonium nitrate, common fertilizer.
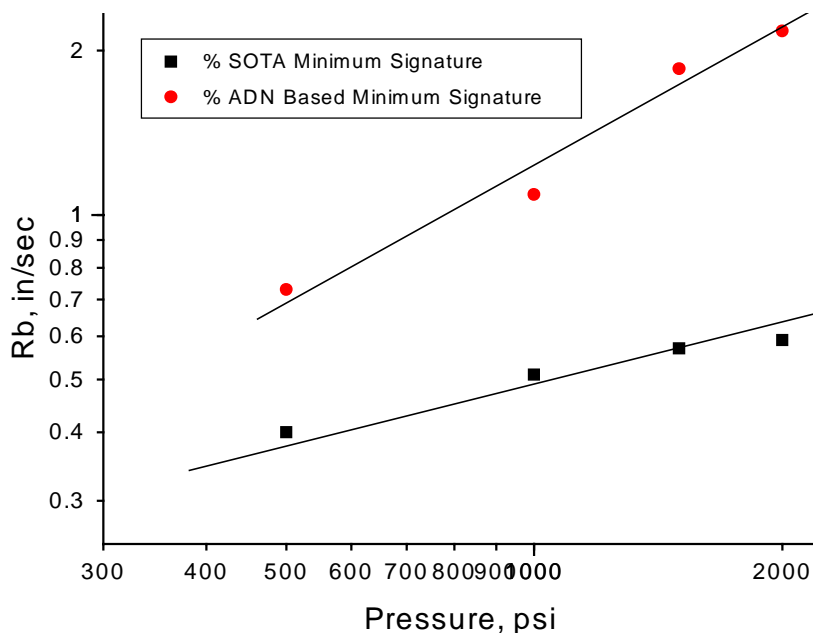

Figure 3   Burning Rate Comparison of ADN Minimum Signature Propellant Versus SOTA

In a scale-up effort, ADN was evaluated as the sole oxidizer in several minimum signature propellant formulations. These formulations consisted of nitrate ester plasticized binders which were based on energetic and non-energetic polymers. Polymers that were evaluated included GAP-polyol, Formrez, and a PEG/PCP combination. Good cures were obtained with both the GAP and Formrez formulations indicating the possibility for acceptable mechanical properties. The study included ingredient compatibility, sensitivity, propellant processability, strand burning rate determination, and small scale 2 inch by 4 inch motor firings.

Additional details regarding the results of lead free propellant formulation research can be found in the papers cited under the publications section.

The toxicology results indicated that for organometallic components, substitute compounds will pose little toxicity hazard by any of the three exposure routes (oral, dermal or inhalation) and have much reduced toxicity when compared with the formerly used compounds of lead. Additional details can be found in CHPPM report 81-9100-99.

<u>Conclusions</u>

Use of bismuth compounds have resulted in the development of new lead-free propellant formulations that meet all performance, ballistic, signature, and aging properties necessary for further evaluation in tactical missile configurations. The preliminary work has been done by the successful test firing of these propellant formulations in 2.75 rocket and TOW motor configurations. Additional prototype motor tests are recommended before large-scale motor production. Toxicological results and literature searches reveal that bismuth is a much less hazardous substance than lead and will pose a reduced health risk to humans and the environment.

Across the range of formulations for ADN propellants evaluated, dramatic enhancements in burning rate were determined. The initial evaluation of ADN in solid rocket propellant has shown that it has potential as a new minimum signature oxidizer. Good propellant cures were obtained with both GAP-and Formrez -based formulations indicating the possibility for acceptable mechanical properties. Although the strand burning rates were primarily determined from micro-mixes which typically do not give the best mixing and provide only enough propellant for an average of three strands at each pressure, the results of the burning rate analyses were quite good, indicating good mix homogeneity.

The GAP/ADN formulations exhibited higher than desired friction sensitivities. Because of this safety concern in the processing and handling of the propellant, GAP was replaced with Formrez to decrease the sensitivity of the formulation. The reduced sensitivity data collected for the Formrez based formulations is also promising. This data, along with excellent improvements to burning rate, resulted in a formulation down-selection to the one-pint mix level. The problem of high end-of-mix viscosity encountered with the 52% ADN one-pint mix will be addressed by particle size blending and increased plasticizer addition in future formulation work. The lower solids (47%) formulation that was used for the 2x4 motor tests processed well and still exhibited a theoretical Isp of 249 seconds. Additional effort is needed to obtain ADN of the proper size and shape.

Based on partial work performed by CHPPM and the literature search performed by AMCOM, it is concluded that bismuth compounds pose a much reduced health risk compared to lead compounds currently used in minimum signature propellants.

Summary

In summary, this research demonstrated that two bismuth compounds, bismuth salicylate and bismuth citrate, can be used as direct replacements for currently used lead compounds without any loss in propellant performance, ballistic, signature, aging and service life properties. Additionally, GAP/ADN formulations show promise in the minimum smoke arena but additional work is necessary before a useable formulation is available.

Transition Plan

Potential users of the bismuth formulation technology are missile weapon systems that use minimum signature propellants. Currently fielded systems include HELLFIRE, Hydra 70 (2.75), TOW II and Javelin. Systems such as these are currently out of production or future production is near term and schedule constraints and re-qualification costs make transition to new formulations prohibitive. Therefore, more likely candidates for these new formulations are weapon systems of the future. The Propulsion and Structures Directorate at AMCOM is currently assessing transitioning environmentally friendly composite formulations and lead free minimum smoke technologies to CKEM and the Common Missile. A Cooperative Research and Development Agreement has been entered into with a private contractor to further evaluate the bismuth lead-free formulations. The goal of this effort is to verify current findings and to determine propellant Insensitive Munitions properties.

There are some other very important factors for considering the bismuth lead-free propellants for next generation tactical missile applications. These formulations can be cured at very low temperatures, typically at less than 100°F. These low temperature cures will eliminate the need for large cure ovens which are maintained at high temperatures to 140°F. Improved propellant mechanical properties and extended propellant service life will be a result of these low temperature cures.

Before ADN can be useful for traditional (i.e. low pressure exponent) solid propellant applications, the issue of ballistics will have to be addressed. Future work will include evaluation of possible ballistic

catalysts since the pressure exponents determined for both the GAP and Formrez formulations were higher than desired.

Recommendations

This program has demonstrated that technology could be put in place to achieve the goals originally established as part of this program. The AMCOM Propulsion and Structures Directorate will continue to explore opportunities to transition the lead free minimum smoke formulations into Army tactical weapon systems of the future. The GAP/ADN formulations extend the possible burning rates of minimum signature propellants by a factor of two, providing ballistic enhancements and energy not currently available for fielded minimum signature systems. Because of its potential, ADN will be evaluated further.

List of Publications

"Analysis of Ammonium Dinitramide (ADN) Procured from Sweden," Technical Report RD-PS-99-8 "D650 Project No. 98101 by Richard C. Hatcher and Robert L. Stanley, February 1999
"High Performance Lead-Free Minimum Signature Propellant Development" by Larry Warren, 1998 JANNAF PDCS and SEPS Meeting, April 21 - 23, 1998.

"High Performance Lead-Free Minimum Signature Propellant Development" by Larry Warren, 1998 JANNAF Propulsion Meeting, Cleveland, OH. July 1998.

"High Performance Lead-Free Minimum Signature Propellant Development" by Larry Warren, 2000 JANNAF PDCS and SEPS Meeting, May 8-12, 2000.

"Evaluation of ADN in Minimum Signature Propellant Formulations" by R.C. Hatcher and R.L Stanley, 2000 JANNAF PDCS and S&EPS Joint Meeting, Cocoa Beach, FL, May 8-12, 2000.

 "Toxicity Review of Proposed Green Missile Components" by Dr. Mick Major, CHPPM Project No. 81-9100-99, May 1999.

U.S. Army Aviation and Missile Command Continued

Develop Environmentally Clean Methods for Processing Energetic Oxidizers

Summary

The liquefied CO_2 antisolvent process has been successfully demonstrated to comminute oxidizers into crystal morphologies suitable for propellant applications. Large and small oxidizer particles can be generated using the liquefied CO_2 antisolvent process. This process has been shown to be highly dependent on solvent selection for obtaining high oxidizer recovery efficiencies and desirable crystal morphology. For AN, ADN, and RDX oxidizers the optimum solvents for particle comminution were determined to be methanol, acetonitrile and acetone, respectively. To generate larger comminuted particles, the antisolvent process was used in reverse to allow for crystal growth. In this case the solvent selection and the rate of addition of CO_2 are the major factors in resultant particle morphology. Test results also have demonstrated that stabilizers can be co-precipitated with oxidizers, multimodal blends of comminuted particles can be generated, and processing solvents can be successfully recycled and reused.

Technical Approach

Research has been conducted at the U. S. Army Aviation and Missile Command (AMCOM) to develop a liquefied gas antisolvent process to produce comminuted oxidizers in a size, shape, and purity suitable for propellant manufacture. The process supports pollution prevention objectives by using carbon dioxide as an environmentally safe liquefied gas as a direct substitute for traditional organic processing solvents. The closed-loop, antisolvent processing method typically involves the following four steps: (1) Dissolution of the solid oxidizer in a suitable solvent, (2) Spraying the oxidizer solution through an atomizing nozzle into liquid carbon dioxide, (3) Recovery of the comminuted oxidizer particles by filtration from the solvent/antisolvent solution, and (4) Evaporation of the liquid carbon dioxide to recover the original solvent.

Accomplishments and Results

A large number of experiments were conducted with the one gallon, polycarbonate laboratory scale apparatus (See Figure 1). The processing parameters and experimental conditions that control this comminution process were evaluated using ammonium nitrate (AN), ammonium dinitramide (ADN), and 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20). These effects were refined using the ten gallon bench scale apparatus (See Figure 2). The effects of solvent, nozzle shape and orifice size, oxidizer concentration, feed rate, and order of antisolvent addition were studied as a means to influence particle sizes and shapes.

The choice of solvents was limited since they must not only dissolve the oxidizer, but also they must be soluble with the liquid CO_2 antisolvent. Different feed stream solvents were found to have a dramatic effect on the morphology of the oxidizer particles. It is believed that the residence time of the droplet in the liquid CO_2 is the main reason for the differences observed from one processing solvent to another.
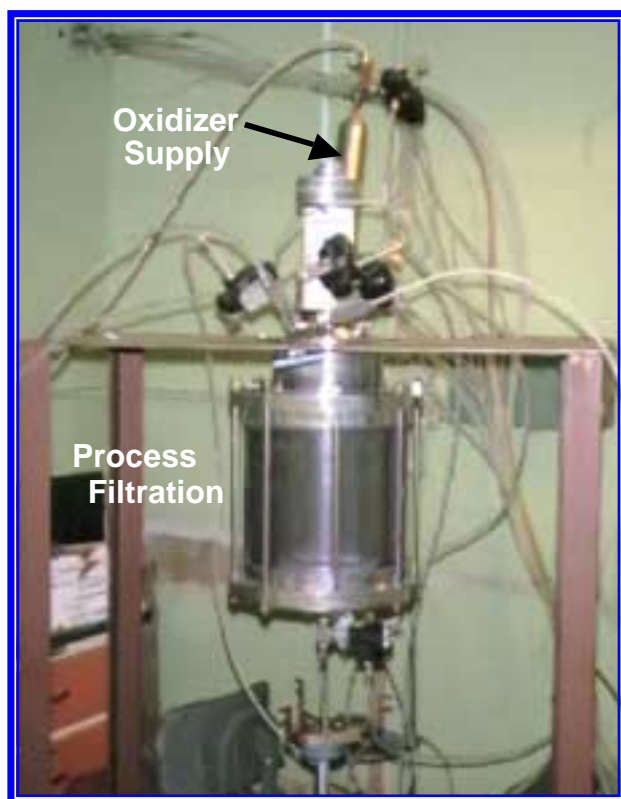
Figure 1   Laboratory Scale

Figure 2   Bench Scale Apparatus

The two types of nozzles tested were fan and impingement. The impingement nozzle (.008 in) was found to produce smaller particles even though the orifice diameter of the fan nozzle (.009 in) was similar. Different orifice diameter (.008 and .08 in) impingement nozzles were explored. No significant particle size differences were observed when increasing, by a factor of 10, the nozzle orifice size.

The concentration of oxidizer in the solvent feed solution was observed to exert minimal influence on the particle size. To minimize the amount of solvent usage, most oxidizer feed solutions were used near saturation. Solutions at saturation had a tendency to precipitate from solution and clog the nozzle orifice before all of the oxidizer feed solution could be fully atomized into the liquid CO_2 antisolvent. The feed rate was controlled by the pressure differential between the oxidizer supply tank and the processing vessel. Feed rate had minimal effect on oxidizer comminution except for AN particles.

AN Particle Comminution

The ionic nature of AN limits its solubility even in polar organic solvents. Solvents used for the AN experiments were methanol and ethanol. AN is five times more soluble in methanol than ethanol; however, the median diameter of the AN particles was smaller when using ethanol as the processing solvent. Other than particle size, no significant difference in crystal type was observed between these two solvents. Since very small particles of AN were not required for propellant formulation, methanol was the solvent of choice based on its greater solubility. Oxidizer solution feed rate was found to be the dominant factor affecting oxidizer particle morphology. Slower feed rates (<.5 l/min) were found to produce optimum AN particles. This is believed to be due to a combination of effects. High feed stream rates can cause accretion (droplet growth) of the atomized oxidizer containing droplets prior to entering the liquid CO_2 antisolvent. Long residence times of oxidizer containing droplets in the liquid CO_2

antisolvent also can allow for agglomeration of droplets or particles. These droplet growth effects are apparently compounded by increases in the oxidizer feed stream rates. It was observed that these effects tend to promote the formation of larger particles (e.g., 50 to 100 m). This effect is shown in Figure 3.
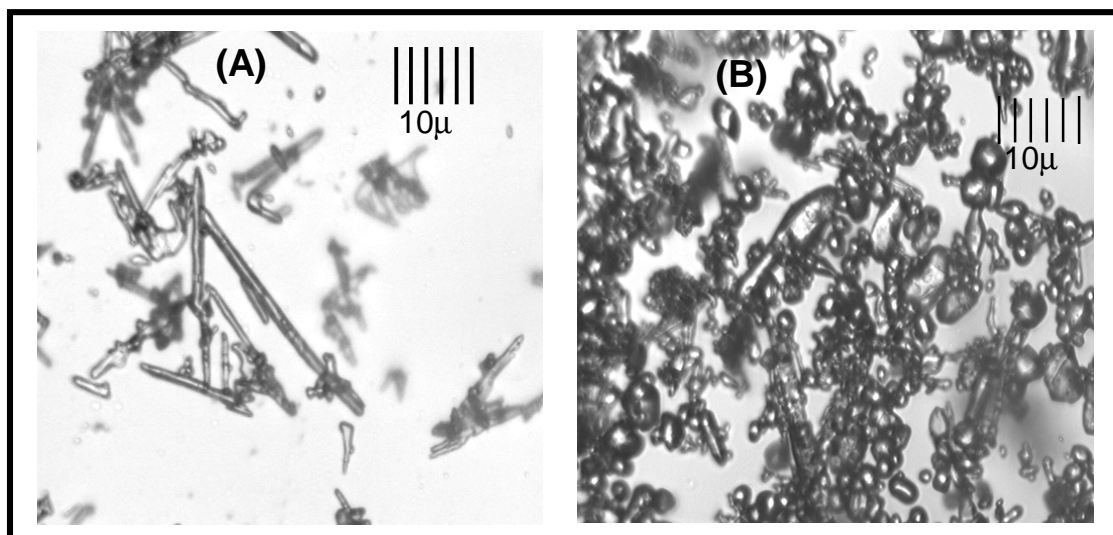

Figure 3   Comminuted AN: (A) high feed rate (B) low feed rate

CL-20 Particle Comminution

The three solvents used to comminute CL-20 were acetone, acetonitrile, and ethyl acetate. Although CL-20 is very soluble in each of these solvents, two different particle morphologies were generated. The particles produced from the acetone feed stream solvent were large (>50 m) and tended to have flat, jagged edges. These crystals were observed to be very fragile and easily broken into fine particles when stirred. In contrast, the comminuted particles generated from acetonitrile and ethyl acetate solutions were observed to be very small (~5 m), flat, rounded crystals (see Figure 4). A laser scattering particle size analysis of the particles from the acetonitrile solution showed two peaks with values of 2.5 and 7.5 m. Scanning Electron Microscope (SEM) pictures of the particles showed that most of the larger particles were actually composed of agglomerated smaller particles.

CL-20 is known to exist in several different polymorphic forms. The preferred polymorph is the epsilon form because of its higher density. IR spectra of the particles produced from this CO_2 antisolvent process showed that the CL-20 particles produced were mainly the alpha polymorph. Thermal analyses indicated that a mixture of two polymorphic forms were present in the comminuted CL-20 oxidizer when acetonitrile was used as the processing solvent. Differential scanning calorimeter (DSC) analyses of these CL-20 particles show a small phase transition from the epsilon to the gamma polymorph during heating. For the majority of the sample, an alpha to gamma phase change is observed. Thermogravametric analyses (TGA) of the comminuted CL-20 samples also detect significant weight losses of up to 8% during the phase changes to the most thermally stable gamma polymorph. To determine the source of this weight loss, small samples were heated in a gas chromatograph attached to a mass spectrometer. The mass spectra of the gases produced indicated that acetonitrile solvent and CO_2 were present during the CL-20 epsilon phase transition, but mostly CO_2 was present during the higher temperature alpha polymorph phase transition. Solvent entrapment is known to occur within CL-20 crystals; however, this CO_2 comminution process appeared to exacerbate the amount of CO_2/solvent that was entrapped within the crystal structure.
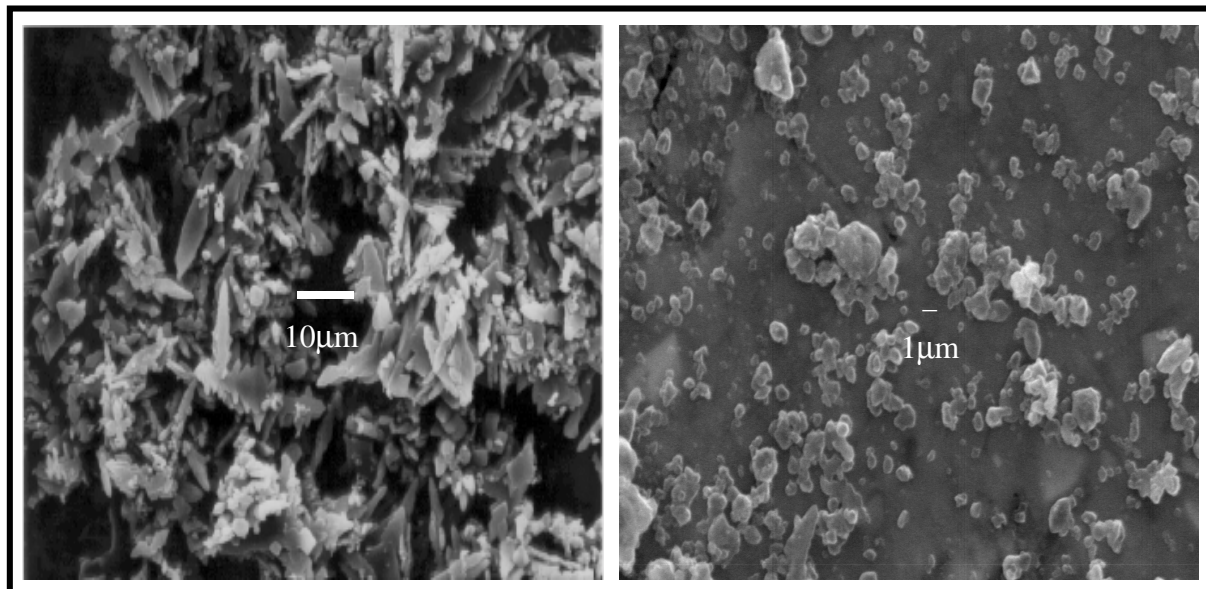
Figure 4   SEM pictures of comminuted CL-20: (A) from acetone and (B) from acetonitrile

ADN Particle Comminution

Similar to AN oxidizer, ADN is not very soluble in any organic solvent. The solvents used for dissolving ADN were the alcohols. 2-propanol was found to produce ADN particles having the most optimal crystal shape. Particles from the 2-propanol solution are more spherical and smaller than those obtained from the ethanol solutions (see Figure 5). A problem that was observed to occur with ADN in either solvent was that the solution does not mix (i.e. slow miscibility) as readily with the CO_2 in comparison to some of the other oxidizer solutions. This means that a significant portion (up to 30%) of the oxidizer can remain in the solvent/antisolvent solution after it is sprayed into the liquefied CO_2. Using solutions near saturation and decreasing the overall amount of solution minimized this effect (<10%).
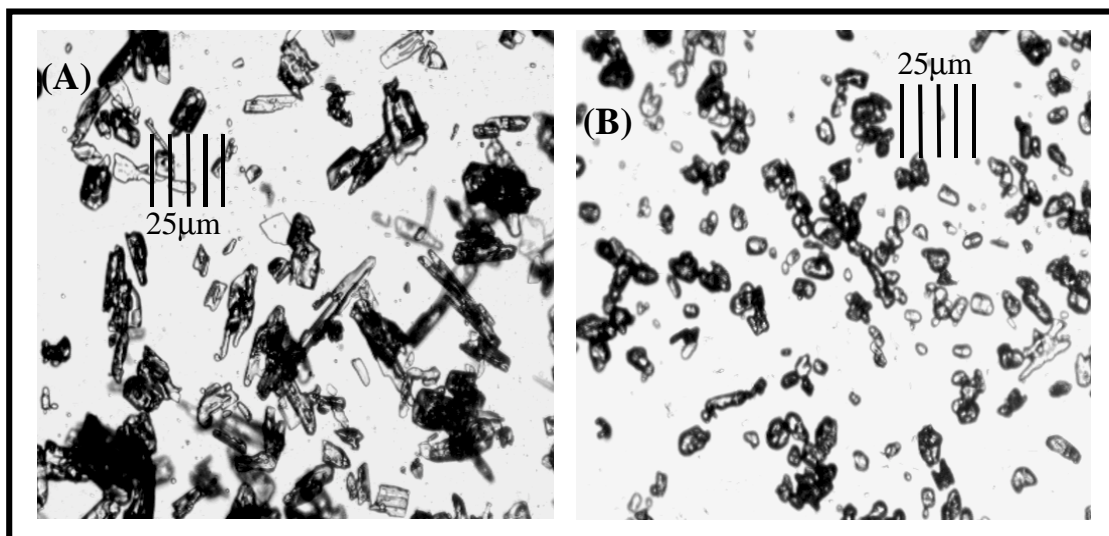

Figure 5   Comminuted ADN: (A) ethanol and (B) 2-propanol

Although alcohols were the initial choice for the ADN solvent, acetonitrile also was tested as the oxidizer solvent. The crystal morphology of the comminuted ADN was as good as that obtained when using 2-propanol as the solvent (See Figure 6). The major advantage of the acetonitrile was that a recovery efficiency of greater than 99% was obtained. The acetonitrile allowed for the addition of a larger quantity of oxidizer solution to the same amount of liquefied CO_2 that was used with 2-propanol. The result was that larger quantities of ADN could be comminuted per batch.
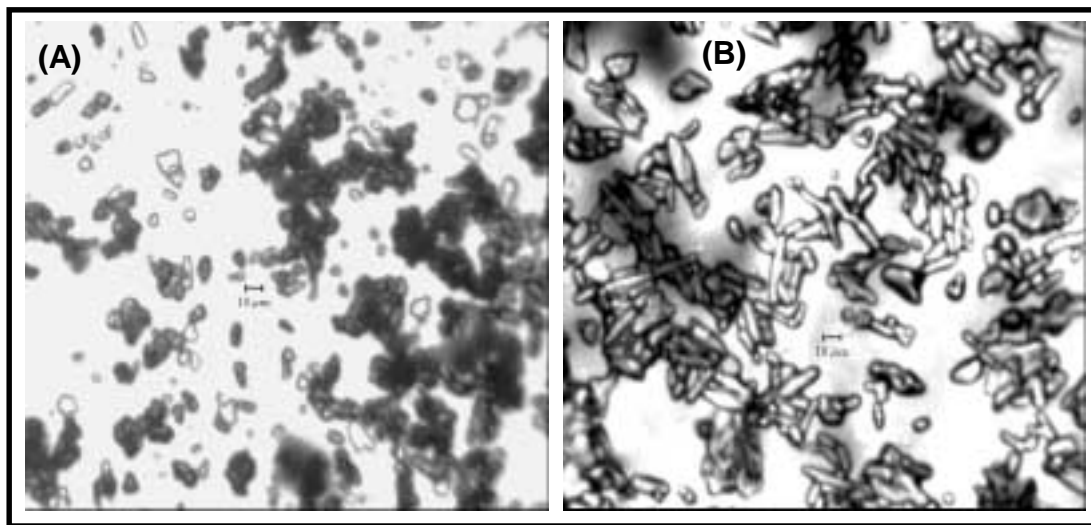

Figure 6   Comminuted ADN from acetonitrile (A) normal process and (B) reverse process

Test results have demonstrated that amine-based, propellant stabilizers can be efficiently co-precipitated with ADN. These stabilizers have the potential to reduce the decomposition of the oxidizer during long-term storage. Co-precipitation of ADN with urea, hexamine, and N-methyl-4-nitroaniline (MNA) was investigated. The stabilizers were dissolved with the ADN in the same solution prior to co-precipitation in the antisolvent. Urea was co-precipitated with ADN in quantities as high as 2 weight percent. Similar results were seen with hexamine. The ADN/MNA mixture was yellow in color. However, according to chemical analysis only trace quantities of the MNA were incorporated.

A series of experiments was performed to generate larger particle sizes of ADN for uses in multimodal propellant formulations. Larger ADN particles (100-300 micron) were obtained using a straight 0.25 inch O.D. tube to add the dissolved oxidizer solution to the antisolvent. The resulting particles were flat and irregular in shape in comparison to those obtained with an atomizing nozzle. To determine if orifice size had any effect on particle dimension, atomizing nozzles, having up to four times larger diameters than previously used, were investigated with ADN. At these larger droplet sizes, only minimal increases in comminuted particles were observed. With the largest orifice size nozzle, small amounts of irregular platelets began to be observed instead of the desired rounded shapes. It was concluded that larger nozzle orifices are not necessarily better for generating rounded, ADN particles. An alternate approach was used in an attempt to generate larger ADN particles. In a reverse process CO_2 was added to the dissolved ADN solution. The resulting particles were various shapes with rounded edges. A large number of the crystals were elongated rods in the 20 to 40µm size range. It is possible that the rate of CO_2 addition to the ADN solution was too fast to generate larger rounded particles. Further experiments are needed to determine whether the rate of CO_2 addition has any influence on ADN particle morphology.

RDX Particle Comminution

The AMCOM CO_2 antisolvent process for particle sizing has the potential of meeting purification and crystallization requirements for recycling energetic materials recovered from rocket motor propellants and warhead explosives. The particle sizing process was evaluated in a series of tests using both virgin and reclaimed cyclotrimethylenetrinitramine (RDX) oxidizer. The reclaimed RDX was previously recovered from obsolete, Army rocket motors. To show that the reclaimed RDX could be reused, a sufficient amount was comminuted for reformulation into a TOW flight motor.

RDX has a limited solubility in organic solvents at room temperature. In these tests acetone, acetonitrile, and DMF were tested as solvents for the RDX. The solvents were evaluated on their ability to dissolve the RDX, to generate the desired particle morphology, and to obtain high recovery efficiency. All of the solvents dissolved about the same amount of RDX. The recovery efficiency of RDX from either acetonitrile or N, N-dimethylformamide (DMF) was 80-90 percent. Acetone was found to produce the best recovery efficiency (>99%). All three solvents produced particles with similar crystal morphology. The particles were found to be a mixture of thin flat crystals and rounded crystals. The flat crystals were <5 microns thick. The rounded particles were 20-30 microns in diameter. Since the highest RDX recovery efficiency was generated from acetone, it was the solvent of choice.

In an attempt to produce larger particles from acetone, several experiments were conducted with different sizes of atomizing nozzles. Using atomizing nozzles up to 0.08 inches in size did not affect the diameter of the RDX particles. Tests also were conducted using a straight 0.25 inch OD tube to spray the oxidizer solution into the liquid CO_2. The particles generated from this approach had the same size and shape at those produced with the atomizing nozzles.

When the comminution process was reversed, larger particles of RDX could be produced. This procedure required adding the oxidizer solution to the process/collection vessel first and then slowly spraying in the liquid CO_2. Both acetone and acetonitrile were used as solvents for this reverse process. The particles produced from acetonitrile were flat (<10 µm) and rectangular in shape. The particles were 100-500µm long. These flat crystals were fragile and could easily be broken into smaller particles (<20 µm). When using acetone, the reverse process generated RDX crystals in the 100-300 micron range. These crystals were hexagonal in shape and approximately 50-75 µm in diameter (See Figure 7).
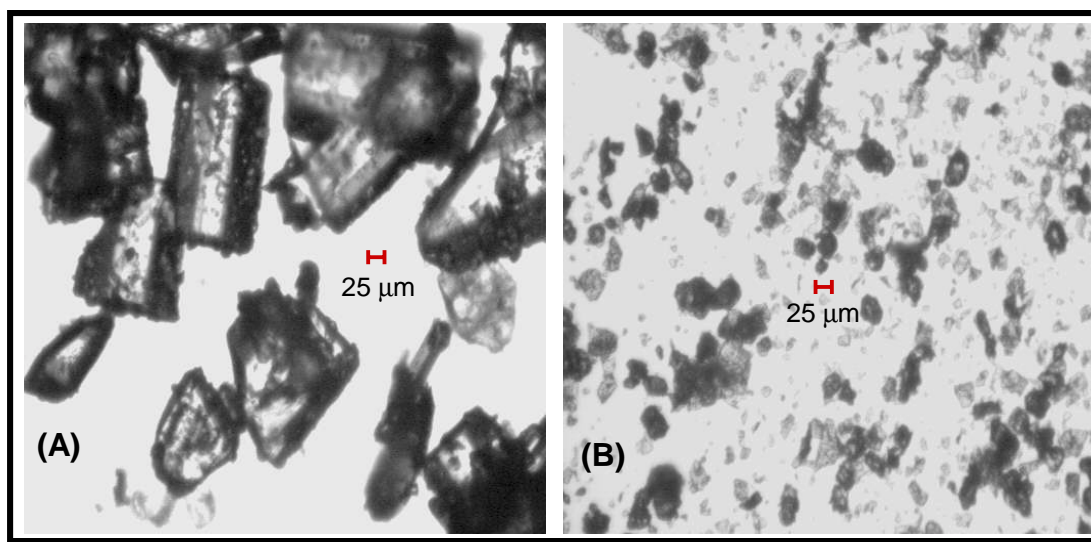

Figure 7   RDX comminuted from acetone by (A) reverse process and (B) normal process

After determining the optimum solvent and operating conditions, several pounds of large and small sizes of RDX were produced. Several significant milestones were successfully achieved during this phase of the effort. These achievements included (1) the comminution of high purity RDX from crude recovery products, (2) the generation of both small and large particle sizes of RDX oxidizer, and (3) the recovery and recycling of the processing solvent. To further optimize the process, two batches of RDX particles were produced per experiment. This was accomplished by comminuting both batches of RDX before performing a final rinse of the particles. Utilizing this procedure saved two gallons of CO_2 that normally would have been used to rinse the first batch of particles. It also saved the time needed to clean out the vessels between each experiment. Combining the reverse process followed by the normal process also produced a multimodal blend of comminuted particles.

Propellant Formulations with Comminuted Oxidizers

AN: Successful propellant mixes were made with the 20-25 m AN particles. The fine comminuted particles appeared to have exceptional mechanical properties in comparison to standard zinc oxide and permalene stabilized AN oxidizers. Low sensitivity (e.g. impact insensitive), moderate performance AN propellants were prepared using energetic, ORP-2 polymer in nitrate-ester-plasticized formulations. These propellants were observed to have excellent cure properties. The observed high integrity of these AN propellants is thought to be attributed to the low moisture content and crystal morphology of the AN derived from the anhydrous CO_2 processing method. Based on the results of these initial formulations, the comminuted AN particles appear to be suitable for use in IM propellant applications.

ADN: The comminuted ADN particles in the 10-20 µm range were evaluated in several high performance, minimum signature propellant formulations using micro (25 gram) and pint scale (300 gram) propellant mixers. Energetic GAP or non-energetic polyethylene glycol/polycaprolactone (PEG/PCP) or Formrez, nitrate ester plasticized propellants were tested. Propellant cure difficulties were observed with the PEG/PCP formulations. Significant specific impulse and consistent burning rate increases were demonstrated with the other two formulations in comparison to current state-of-the-art propellants. Based on these preliminary test results, the ADN generated from this liquid CO_2 antisolvent process appears to be suitable for meeting propellant processing requirements in terms of dryness, morphology, and purity.

The extreme hygroscopic nature of fine AN and ADN particles will always present a processing challenge for propellant formulators. The anhydrous, liquid CO_2 process does produce very dry oxidizer particles. It is this aspect that makes the CO_2 process particularly appealing for use with hygroscopic oxidizers. The anhydrous conditions associated with this liquid CO_2 antisolvent method virtually assure that ADN and AN-containing propellants can be formulated with a higher degree of consistency and should demonstrate improved mechanical properties.

CL-20: Several attempts were made to manufacture CL-20 propellants using the comminuted particles. A major problem was observed in that the propellants did not produce acceptable cures. Initial assessments suggested that catalytic surface affects on finely comminuted particles (e.g., 2 m) were adversely affecting the isocyanate cure process by generating deleterious gas generation. Alternatively, the observed gassing during propellant curing could be a direct result from the release of entrapped CO_2/solvent from the interstitial sites in the CL-20 crystal. It was clear from AMCOM investigations that the release of entrapped CO_2 and/or solvent molecules from the CL-20 crystals was not thermally induced. Based upon extensive thermal testing with comminuted CL-20 samples, it was concluded that the release of entrapped solvent and/or CO_2 must be solubility induced. It is speculated that the CL-20 has a tendency to solubilize in one or more of the liquid propellant plasticizer or polymer ingredients.

RDX: The comminuted RDX was successfully evaluated in a minimum signature propellant formulation. Several pounds of small (20-30 m) and large (100-300 m) particles were comminuted from the reclaimed RDX using the CO_2 antisolvent process. Pint-sized propellant mixes with the comminuted RDX particles were prepared and evaluated. Direct comparisons between the reclaimed, comminuted RDX and fluid-energy milled, virgin RDX oxidizers were made by preparing samples using the same propellant formulation. Propellant ballistic, mechanical, and burn rate data for these formulations were determined to be virtually identical. For further evaluation of the reclaimed, comminuted RDX, full-scale TOW motor castings were prepared (See Figure 8). One motor was formulated with reclaimed RDX that had been comminuted using the liquid CO_2 antisolvent process. The other motor was prepared using virgin RDX that had been fluid energy milled. Static firings of both of the full scale TOW motors showed that the propellant ballistic, mechanical, and burn rate data were virtually identical (See Figure 9).

Figure 8   Full scale TOW motors
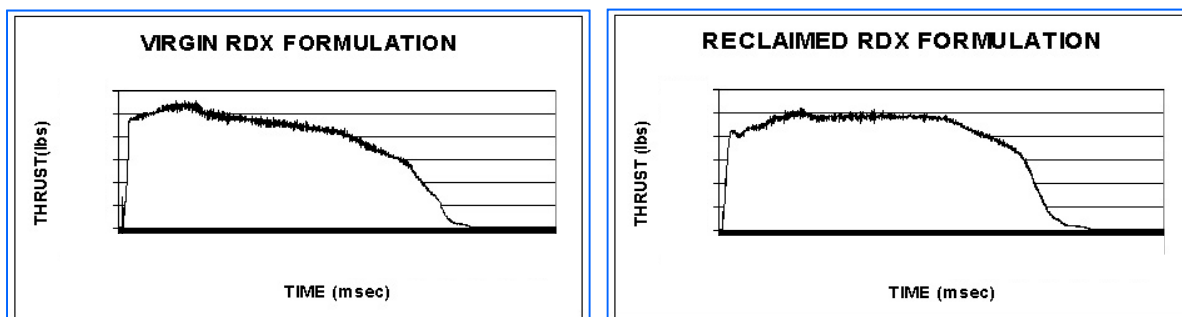

Figure 9   RDX burn rate data

<u>Conclusions</u>

A process has been developed that supports DoD Green Missile pollution prevention objectives by using an environmentally safe, liquefied gas as a substitute for traditional, liquid organic processing solvents. Substitution of a liquefied gas antisolvent for conventional organic solvents reduces the total volume of volatile organic compounds used in chemical purification and particle processes. Another benefit of the process is the ease by which the oxidizer solvent can be recovered from the liquefied gas for recycle and

reuse. Oxidizer comminution using the anhydrous, liquid CO_2 process produces very dry particles, which makes this process particularly appealing for use with hygroscopic oxidizers.

Transition Plan

The liquefied CO_2 antisolvent process has successfully been transitioned from the lab scale to the bench scale during the SERDP funded Green Missile program at Redstone Arsenal. The continued development of this technology requires the further scale up from current bench scale, pound quantities to a pilot plant configuration capable of generating hundred pound quantities per day of comminuted oxidizers. From a chemical process engineering perspective, this technology is best applied to the comminution of hygroscopic and soft crystalline materials that are not amenable to traditional fluid energy milling processes. The application of this technology for the comminution and purification of the ADN and AN oxidizers for rocket motor propellants was demonstrated. When propellant formulations using these oxidizers are developed and matured, this antisolvent process will be capable of producing particles in the required sizes and morphology. The limiting factor affecting the near-term transition of this technology is the lack of progress by the propulsion communities to overcome the ballistic and formulation challenges associated with these materials. When these challenges are overcome, this antisolvent, comminution technology will be available to meet the requirements for generating the ADN and AN oxidizers.

Alternatively, this technology could be used to purify and comminute recovered HMX and RDX oxidizers generated from the existing AMCOM pilot-scale Missile Recycling Capability (MRC) at Redstone Arsenal. The current facility reclaims HMX and RDX oxidizers from obsolete propellants and warhead explosives at the hundred pound per batch quantities. Although these recovered oxidizer materials are ~99% pure in their crude form, they require further purification and particle size communition to meet military and commercial reuse applications. Currently, these recovered oxidizers are being provided to the Holston Army Ammunition Plant for particle communition using traditional recrystallization methods with acetone and cyclohexanone solvents. Because of the availability of the existing, excess production capability at the Holston facility, it is not economically prudent to develop a competing crystallization capability for the recovered HMX and RDX oxidizers. However, if this capability were available today, it would be used to generate high purity, comminuted HMX and RDX

Recommendations for Technology Implementation

The execution of this transition plan will require the purchase and installation of the following major components: (1) a commercial sized liquefied gas recompression unit for recovering the CO_2 process solvent, (2) two 200 gallon capacity stirred processing vessels, (3) one 50 gallon oxidizer supply tank, and (4) ancillary system support equipment to include valves, instrumentation, and etc. When funds become available to support the acquisition of the required system components at the pilot-scale, the technology transition plan can be implemented.

List of Publications

"Particle Communition by Liquefied Gas Antisolvent Processing" by, Joseph K. McDonald, Jeffery S. Wright, and William S. Melvin, 1998 JANNAF PDCS and S&EPS Joint Meeting, April 21-23, 1998. CPIA Pub. 674, Vol. II, pp 83-92.

"Liquefied Gas Antisolvent Particle Communition Processing" by Jeffery S. Wright, Joseph K. McDonald, and William S. Melvin, 2000 JANNAF PDCS and S&EPS Joint Meeting, Cocoa Beach, FL, May 8-12, 2000, CPIA Pub. 698, pp 201-209.

Develop Lead Free Extrudable Propellant for Minimum Smoke Systems

Technical Approach

State of the art technology for extrudable propellant systems, have been limited to double-base propellants due to their properties inherent of a thermoplastic as a result of their method of manufacturing. These propellants use an energetic plasticizer, such as Nitroglycerin (NG) and the energetic polymer Nitrocellulose (NC). It is also these materials that enable the propellant to be classified as smokeless (minimum signature). The process begins by preparing a slurry of NC in water and transferring the nitrate ester by eduction. The water-wet paste, as it is called, is formulated with ballistic (burn-rate) modifiers in a horizontal mixer and then processed on a series of rollers that force the plasticization of the NC fibers with the nitrate ester. Historically the ballistic modifiers employed are some type of a lead or copper compound. The final rolling process produces a thin sheet of propellant that is ultimately extruded to the shape and size of the grain required for the given rocket motor. This type of propellant becomes limited in its application to larger diameter grains due to cracking as a result of the extrusion process. For the most part extruded double-base propellants have a maximum diameter of 4 - 6 inches. The extruded grain is then placed in ovens for annealing which releases the stress induced by extrusion. Given this brief depiction of the process for double-base propellants one may extrapolate the associated environmental effects.

There are three areas of concern regarding the environmental impact that these propellants incur. First is the process water, second is the lead used in the formulation and third is the annealing process. With respect to the process water, NG has a solubility of 1.8 grams/liter at 20 °C and 2.5 grams/liter at 50 °C[1], which occurs readily during the paste manufacturing process. At the Naval Surface Warfare Center Indian Head Division (NSWCIHD) the primary concern focuses on reducing the level of nitrate ester to a point well below its saturation such that it does not become a safety hazard. This level has been set at 1000 ppm by the Indian Head Safety Department. Additionally due to the Federal Agencies' Chesapeake Ecosystem Unified[2] Plan the station has agreed to a reduction of nitrogen[3] in the wastewater that is discharged to the tributaries of the Chesapeake Bay. Current practice at the Biazzi and Moser Nitration Plants enable both of these criteria to be satisfied and are also adaptable to double base paste manufacturing. On the second issue regarding the use of lead it is estimated that at previous production of the 2.75" rocket motor and other double base propellants thousands of pounds of a leaded ballistic modifier are used in formulations. Assuming a 200,000-pound annual production of the 2.75" motor with a nominal 4% leaded ballistic modifier, then 8,000 pounds of this compound would be required. Previous efforts have led to the development of various copper and bismuth compounds as replacements for ballistic modifiers, however none have equaled the effect that lead has on plateau and mesa burning at low pressures. And finally the third issue regarding annealing of double base propellants is concerned with nitroglycerin air emissions.

Current requirements for new facilities at NSWCIHD require that air emissions be addressed as part of the processing of energetic materials. With the MILCON of a new annealing facility in place a technology was sought out to treat the nitroglycerin vapors that are emitted. One such technology was photocatalysis of the air stream[4], which employed the use of UV-lamps and titanium dioxide (anatase). In considering the impact that double base propellants incur it was desired to develop a formulation that would not create waste streams as discussed with manufacturing double base paste and annealing of the extruded grains. The use of pelletized nitrocellulose (synonyms: plastisol nitrocellulose and PNC) and butanetriol trinitrate (BTTN) as alternates to NC and NG does not incur an air or water emissions problem and would thus allow the program to focus exclusively on replacement of lead.

Propellant formulations have been investigated as a replacement for the AA-2 double-base minimum-smoke propellant used in the Mk 66 2.75" rocket motor. This propellant contains a lead-copper ballistic modifier. The goal of this effort is to develop a lead-free, high energy, extrudable, minimum signature propellant that will replace the AA-2 formulation. Efforts have focused on the development of plastisol nitrocellulose (PNC)/butanetriol trinitrate (BTTN) double base propellant.

Materials
The energetic materials RDX, PNC, BTTN and NC were available in the inventory and the primary ingredients for the PNC/BTTN formulations. The PNC and BTTN were produced on-site and readily available. PNC is the plastisol form of nitrocellulose, which is defined as a finely divided suspension of polymer in a plasticizer. Ethyl centralite (EC) has been added as a stabilizer at a nominal 2%, which is the limitation given by the product specification[5] that it is manufactured to. The NC used to manufacture the PNC was pyrocellulose grade A. PNC is typically stored either heptane or water wet and is dried at approximately 120 -140 °F the day before formulating. The BTTN[6], an energetic plasticizer, is synthesized and then formulated with the stabilizer 2-nitrodiphenylamine[7] (2-NDPA) to 1%. A desensitizing solvent is added to the BTTN at the 20 - 40% level for storage purposes. The solvent employed has either been methylene chloride or acetone. The NC used for formulations was pyrocellulose grade A and stored alcohol wet. The alcohol content is typically 26%. NC was used both in the alcohol wet form and dried. Weight adjustments were calculated to consider the quantity of alcohol in the NC. The RDX used had a particle range as given in Table 1 and satisfied the requirements of Class 5[8] particle size granulation.

The inert plasticizer triacetin (glyceryl triacetate)[9] was used as provided by the manufacturer Eastman Chemical Company. A variety of materials were explored to effect ballistic properties for the PNC/BTTN propellant formulations. These materials included carbon black, organic-copper salts, organic-bismuth salts, bismuth-strontium-calcium-copper Oxide (Bi-Sr-Ca-Cu oxide), bismuth stannate ($Bi_2Sn_2O_7$) and titanium dioxide (TiO_2-anatase). Columbian Chemical Company provided Carbon Black samples. The monobasic copper resorcylate (MBCBR) and copper salicylate were supplied through Shepherd Chemical Company. The MBCBR was received as a water wet pressed cake. It was dried and broken-up using a jar mill with zirconia and burundum grinding media. Microtrac analyzers were used for performing particle size analysis of the MBCBR[10]. Copper salicylate was supplied as a dry powder and its particle size analysis[11] was determined by Microtrac. A number of organometallic modifiers were provided by OMG Americas which included 12% Copper CEM-ALL, 6% Copper NAP-ALL, CATALYST 320 and CATALYST 315. The 12% Copper CEM-ALL comprises copper esters of 2-ethylhexanoic acid, propanoic acid and neodecanoic acid in a 32% mineral spirits solution. The 6% Copper NAP-ALL is the copper ester of naphthoic acid in a 33% mineral spirits solution. CATALYST 320 is the bismuth ester of 2-ethylhexanoic acid in a 26% mineral spirits solution. CATALYST 315 is a mixture of the bismuth ester of neodecanoic acid and 25% neodecanoic acid solution.

Composite propellant formulations investigated the explosive CL-20 and ground (20 - 30 micron) ammonium nitrate with a plasticized inert binder. CL-20 was used in various particle size ranges. The plasticizer is dioctyl adipate and the binder was either Hycar 4404 or HyTemp 4454. Hycar 4404 and HyTemp 4454 are acrylic copolymers of ethyl acrylate, butyl acrylate or other acrylic ester monomers and were produced by B.F. Goodrich and Zeon Chemicals. Ethyl acetate was used as a solvent for reducing the viscosity of the Hycar and HyTemp polymers. Inclusion of a monomer with an active site built into the polymer backbone allows cross-linking to occur with isophorone diisocyante (IPDI) or methyl aziridinyl phosphine oxide (MAPO)/ERL-0510 epoxy resin. Iron naphthanate is used as a cure catalyst for the HyTemp/MAPO/ERL-0510 binder. No catalyst was used for the Hycar 4404/IPDI binder. Graphite, carbon black, Cab-O-Sil (fumed silica), fumed aluminum oxide and lecithin are used as processing aides and to an uncertain extent as burn rate modifiers. Lecithin is primarily a processing aide.

A baseline formulation excluding these compounds has not been investigated for their effects on burn rate.

Methods of Processing - PNC/BTTN Propellant

Three types of mixing equipment were evaluated for preparing PNC/BTTN propellant formulations. Primarily a 1-pint or 1-gallon vertical mixer processed the PNC/BTTN formulations. Other processing techniques included evaluation of a horizontal mixer, in attempt to gel NC with the BTTN solvent, and high shear mixing was explored on the laboratory scale. Addition of ingredients with the vertical mixing began with 2-NDPA, which was ground using a mortar and pestle to facilitate faster dissolving with the BTTN solvent. After addition of the 2-NDPA, the BTTN solvent was added. The BTTN was mixed under vacuum at a bowl temperature up to 140 °F. A dry ice/acetone trap was used in the vacuum line to collect the desensitizing solvent (acetone or methylene chloride) and to insure BTTN would not travel to the vacuum pump. The solvent was considered completely removed when full vacuum was achieved. At this point the bowl temperature is reduced to 100 °F and the plasticizer triacetin and the first portion of PNC are added. PNC is added in three increments. It is important that acetone be completely removed prior to addition of the PNC. Acetone will gel the PNC and change the mechanical properties of the propellant. Ballistic modifiers are typically added with the last addition of PNC. RDX and NC were added in the final addition cycle. The apparent end of mix viscosity was considerably greater for formulations containing RDX and NC. Very fluid formulations were often observed having the appearance of certain ingredients separating.

The propellant was cast into Velostat plastic lined tubes and pans. The propellant was then placed in an oven at 140 °F and allowed to set-up (plasticize) for a minimum of 1-week. After this time the propellant tube samples would be extruded on a heated 2" press through a 0.25" die to make samples for strand burn rate (SBR) testing. Figure 1 depicts extruded strands.

Figure 1   Extruded PNC/BTTN Mix IH940-97J-PNCBT-Z401

Cross-sectional cuts of the propellant pan samples were made with a guillotine and JANNAF Class C dog-bones were prepared (Figure 2). Stress, % strain and modulus measurements were made using an Instron Series IX Automated Materials Testing System. Data was collected at the rate of 20 pts/sec. and the samples were pulled at a crosshead speed of 2 in./min. Durometer Shore A hardness measurements were also determined.

Figure 2   Cross-sectional cut of PNC/BTTN Mix IH940-97J-PNCBT-Z401

The formulations evaluated for the first two years of this project focused on adding NC in its fibrous state as depicted by Figure 2. For the final year, formulations were prepared in which the NC was dissolved into the BTTN solvent. Two methods were explored to facilitate the solution of NC/BTTN solvent. One method was to prepare a premix of the NC/BTTN solvent prior to the day of the mix. The ingredients included the 2-NDPA, triacetin, NC and BTTN solvent. The materials were allowed to sit undisturbed in covered containers at least a day prior to the mix. The other alternative was to prepare the mix in a horizontal mixer. Another approach that was never explored for the NC/BTTN solvent premix was the high shear mixer shown in Figure 3.

Figure 3   Laboratory High Shear Mixer

The high shear mixer was however used to prepare laboratory size PNC/BTTN mixes.

Thermal Analysis
Du Pont's DSC 2910 was used to evaluate thermal compatibility of energetic materials with other ingredients, i.e. burn rate modifiers. Table 1 provides guidelines for approval of materials to be used in formulations. Acceptable changes in the peak exotherm are typically no more than a 10 °C depression from the primary energetic component.
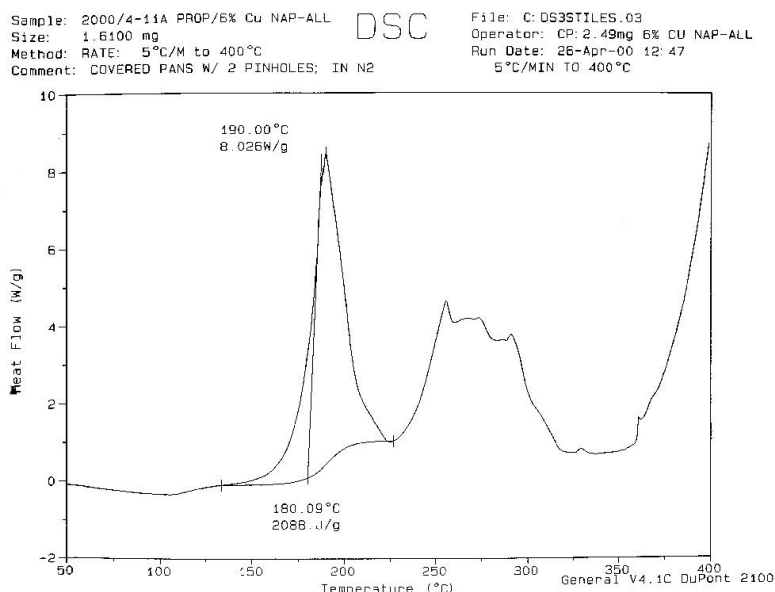
Table 1. Compatibility Guidelines for Admixtures Based on DSC and TGA Data[12].

Degree of Incompatibility	DSC Peak maximum, °C Δ (mixture - ingredient)	TGA Δ (% mixture-% ingredient)
None	0 - 4	0 - 4
Slight	5 - 9	5 - 9
Small	10 - 19	10 - 19
Moderate	20 - 29	20 - 29
Large	>30	>30

The following DSC scans represent a hand mix of the primary energetic materials PNC/BTTN.
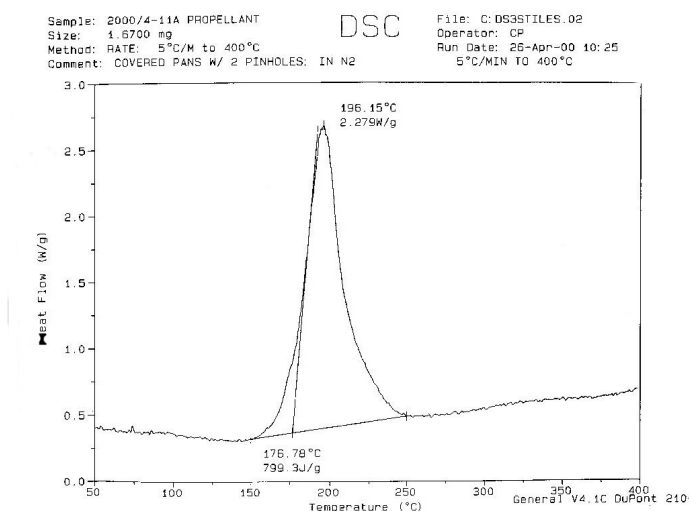
With the peak exotherm occurring at 196.15 °C for the PNC/BTTN a 6 °C change is observed when mixed with the ballistic modifier 6% Copper NAP-ALL.

Sample: 2000/4-11A PROP/6% Cu NAP-ALL   DSC   File: C:DS3STILES.03
Size: 1.6100 mg   Operator: CP: 2.49mg 6% CU NAP-ALL
Method: RATE: 5°C/M to 400°C   Run Date: 26-Apr-00 12:47
Comment: COVERED PANS W/ 2 PINHOLES; IN N2   5°C/MIN TO 400°C

However notice that during such testing an exuberant quantity of material (2.49 mg) with respect to the PNC/BTTN (1.61 mg) is mixed in. This must also be considered when considering true compatibility based on actual concentrations in the formulation. Thermal gravimetric (TGA) techniques could also be employed in which a weight change is the criteria for compatibility. Additional thermal techniques employed to a lesser extent were vacuum thermal stability (VTS). This is a technique whereby the material is heated to a specific temperature and the off-gas is measured within a 48-hour period.

Accomplishments and Results

Historically formulations and processing of double base propellants have focused along two distinct avenues. First is the solvent type propellant used for making casting powder, which in turn is used for making cast double base propellants. Secondly is the solventless extruded process described within this report. And now a third formulation and processing type can be included as an alternate to the solvent and solventless formulations, which is now known as the Alternate Feedstock (AF). AF provides to the formulator a method of producing double base propellants without the use of solvents for both extrusion and cast applications, thus allowing rocket motors of various sizes (diameter) to be manufactured using a double base formulation. During the course of this program efforts were focused on the extrusion conditions that would produce grains with acceptable surfaces. AF still utilizes a nitrocellulose/nitrate ester formulation but one that produces totally different mechanical properties. The nitrocellulose in its plastisol form is commonly referred to as PNC. The PNC plasticized propellants are non-crosslinked rubbery materials. The fact that they are not crosslinked allows more flexibility for extruded processing. Because of their rubbery nature these propellants have better elastic properties at low temperature. The most common propellant for low temperature applications has been a composite type with a polybutadiene (PB) backbone in the binder system. Although AF is likely not to provide similar mechanical properties as PB or replace PB formulations, it may however open doors for propellant variants of a rocket motor system that is looking for attributes such as smokeless, stable combustion (plateau and mesa burning) and environmentally sound formulations.

One of the key attributes to the AF propellant evaluation has been replacement of lead with copper and bismuth organometallics. A number of new compounds were evaluated and shown to give considerable

improvements for faster burn rates from the non-catalyzed formulations. Also these compounds were shown to improve burn rates from materials that were used early on in the project.

Within in the area of processing AF formulations, investigations have led to a number of techniques that show promise in their ability to produce unique materials that are less hazardous from an explosive safety perspective. Also these methods may allow reduction of hazardous materials used in manufacturing some key ingredients such as PNC. For example the high shear mixing process has shown that a fully plasticized PNC with the nitrate ester is possible. This could eliminate the use of heptane in the manufacturing of the PNC as well as its drying operation. The PNC is commonly used in the PBXN-103 explosive in which it is plasticized by trimethylolethane trinitrate (TMETN) and triethyleneglycol dinitrate (TEGDN). Over the years the PNC has shown problems with its ability to be plasticized during the quality assurance testing and in the manufacture of the explosive. High shear mixing would be a means to eliminate this recurring problem. Also because of this technique, applications in the area of gel propellants can be sought. By taking advantage of the fluidity of gels, application in the area of start/stop motors such as terminal guidance thrusters becomes more feasible. A variation of the AF propellant may have attractive attributes preferred over liquid based propellants. And finally there may be some possibility of developing thermoplastic elastomer (TPE) with this type of processing using AF formulations. The attractiveness with TPE's is the ability to recycle energetics by melting and then extruding it into another form for a different system. Many TPE's commercially available are simply a blend of a thermoplastic and an elastomer. This may also be accomplished with AF formulations by using less PNC and more NC. The propellant would be processed by a high shear mixer and then rolled into sheetstock. This project began evaluating this type of formulation and it showed considerable improvement on sensitivity with respect to impact and friction. However the material was never processed on the roll mills.

Summary

Continued research should focus along two avenues. The first being scale-up of the PNC/BTTN processing using both vertical and high shear mixing equipment. This would focus on extruding and test firing a full size motor. Secondly, efforts should evaluate the PNC/NC/BTTN formulation that would be processed by a high shear mixer and rolled into sheetstock. An additional note, which is explained later in the conclusions are the production of butanetriol (BT). For AF formulations to be viable improved scale-up methods will have to be sought.

Conclusions

The primary attractiveness to AF propellant is the ability to produce double base formulations for either cast or extruded processes. Thus, allowing rocket motors of various sizes (diameter) to be manufactured. This also provides a system that is minimum signature and greater stability in combustion. However the economic feasibility is likely to deter program managers to replace conventional double base formulations with AF. The reason is primarily the cost of the energetic materials. BTTN's cost is dictated by its raw materials, specifically butanetriol. Compared to nitroglycerin, BTTN is almost ten times in cost. Nitrocellulose is also considerably cheaper than in its plastisol (PNC) form, mainly because of additional labor cost for processing.

Transition Plan

Formulations based upon PNC/BTTN have significant interest as high energy, low sensitivity minimum smoke propellant. The solventless extrusion process and the absence of lead salt ballistic modifiers make these formulations very attractive. Currently the relatively high cost of butanetriol, the precursor for BTTN, and the limited availability of PNC are hindering further propellant development. Other programs

are in place that target reducing the cost of butanetriol. The results of these projects will also drive the interest in PNC/BTTN. Meanwhile the AF formulation should evaluate other energetic plasticizers such as nitroglycerin, trimethylolethane trinitrate, triethyleneglycol dinitrate, diethyleneglycol dinitrate, butyl NENA and methyl/ethyl NENA.

Recommendations

Evaluation of other energetic plasticizers previously mentioned would provide the necessary energy for the required Isp. Combinations of these materials are likely to be needed to give the desired energy. This can be accomplished by performing some theoretical trade studies using PEP. Also some laboratory work and scale-up to 1-pint mixes will verify the ability to process this material with similar mechanical properties and ballistic properties that are achieved with BTTN. The NC/PNC/plasticizer formulations, for processing on the differential and even speed roll mills, should be investigated as the potential for creating a TPE is attractive.

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Naval Air Warfare Center

Develop Lead-Free Castable Propellant for Minimum Smoke Systems

Develop Complete and Clean, HCl-Free, Combustion of Propellant

Technical Approach

For decades, double-base propellants have fulfilled the need for minimum smoke propellants in many tactical systems; however, they contain 4 to 6% lead catalysts, which presents an environmental concern. The current focus is on propellants that contain no lead catalysts and yet still meet the ballistic requirements of these systems.

In addition to double-base propellants, AP formulations also represent a high percentage of existing propellant mixes. By-products of AP combustion include ozone depleting hydrogen chloride and chlorine gases and thus require alternative oxidizer replacements.

Ammonium nitrate (AN) can be an excellent oxidizer because it imparts the propellant with desirable low shock sensitivity; however, AN can also negatively affect propellant burning characteristics. China Lake has found that energetic oxidizers such as cyclotetramethylene tetranitramine (HMX), cyclotrimethylene trinitramine (RDX), hexanitrohexaazaisowurtzitane (CL-20) and triaminoguanidium nitrate (TAGN), when used in conjunction with AN, produce reasonably good combustion behavior. Ammonium dinitramide (ADN) is a very powerful oxidizer that theoretically could also replace ammonium perchlorate in high performance compositions thus eliminating toxic HCL from solid rocket motor exhaust. Preliminary results also indicated that ADN propellants do not need lead catalysts for good combustion. Additionally, for disposal, ADN can be easily degraded to ammonium nitrate by exposure to light.

Propellant samples containing a combination of CL-20 and ADN have been selected for development. Because of its higher oxygen balance ADN has the potential of increasing propellant performance over that of propellants containing CL-20 as the single oxidizer. On the other hand, CL-20 has a higher density than ADN and, therefore, can increase the propellant density. Thus a combination of CL-20 and ADN could result in a minimum-signature, lead-free propellant with the highest density impulse to date. The calculated specific impulse (Isp) for CL-20/ADN formulations is in the range of 260-265 seconds, which is substantially higher than the Isp of 246 seconds offered by conventional minimum signature propellants.

Through a CRADA, the Chemical System Division of United Technologies (Pratt and Whitney) and NAWC/CL share technologies regarding ADN prilling. CSD has been working on ADN technology through the Integrated High Payoff Rocket Propulsion Technology Program. Sharing technologies is beneficial to both parties.

In another approach to obtain HCl-free combustion products, ADN is also employed as the oxidizer for UFAL (ultra fine aluminum). Several types of aluminum were selected for study including: ALEX (exploded aluminum-Russian), NAWCWPNS nano-aluminum and spherical aluminum (Valimet Inc.). While many oxidizers fail to efficiently combust aluminum, ADN exhibits good properties in this regard.

Since ADN , CL-20 and UFAL are relatively new ingredients for weapon system use, their basic chemical and physical properties as well as their formulation and combustion properties are among some of the basic details that needed to be explored in this program.

UFAL/ADN propellant compositions were chosen for evaluation using low-solid content and energetic plasticizers to give highly efficient and clean burning propellants while meeting performance

requirements. Issues to resolve include ingredient purity and batch-to-batch variations, binder composition, efficiency of aluminum combustion, combustion product composition, pressure and temperature sensitivity of burn rate, and aging. In collaboration with the Air Force Research Lab (Edwards AFB), UFAL was characterized to determine particle size distribution, particle shape, and surface area.

Accomplishments and Results

Recently, prilled ADN material became available to China Lake from CSD through a Navy funded propulsion technology program. When these prills were used in the propellant mixes, it improved the processability by lowering the viscosity and enhanced the flowability of the mixed propellant. However, propellant made with this material tends to be slightly more sensitive in impact tests than the ones made with neat ADN crystals.

There have been some safety concerns about ADN and CL-20 melt mixtures; the Swedish scientists informed us that when ADN and CL-20 melt together they form some unknown compound, which was shown to be very sensitive toward impact and friction. Since we started to formulate minimum signature propellants with a mixed oxidizer of ADN and CL-20, we decided to investigate this problem in further detail.

Mixtures of ADN and CL-20 at 1:1, 2:1, 3:1 and 5:1 weight ratios were mixed together, then subjected to DSC testing. After the melting of ADN at 93°C (indicated by a sharp endotherm), we typically see exotherm onset at 155°C, which is the start of decomposition of ADN and exotherms at 189 and 250°C for the decomposition maxima of ADN and CL-20 respectively.

In all of the DSC results, China Lake did not observe any additional new peaks (other than those we have identified in the above paragraph), neither have we observed any onset or peak temperature changes, which could be contributions from some chemical reaction between ADN and CL-20.

While ADN and CL-20 melts could be sensitive mixtures, this problem does not appear to apply to propellants with mixed ADN and CL-20. Simple physical mixtures of ADN and CL-20 in propellant binders do not contribute to enhanced sensitivity problem. Minimum signature propellants made with ADN and CL-20 were subjected to aging at 70°C for 2 weeks, this is to give ADN and CL-20 a chance to diffuse together, to allow a chance for them to react. We examined the friction sensitivity of unaged and aged propellant samples and we did not observe any difference between these two samples, thus we concluded that no sensitive compound formed during heating these mixtures.

Several series of propellants containing AN/RDX, AN/TAGN or AN/CL-20 in an energetic binder were prepared in an attempt to demonstrate their high chemical energy and good combustion properties.

Work has continued with two propellant candidates, ORP 2A/BTTN/ CL-20/ ADN and ORP 2A/BTTN/ ADN with special emphasis on burn rate characterization over a wide pressure range (500 to 8000 psi) and processing properties with different ADN prills.

Both of these behaved quite similarly showing a desirable burn rate of 0.8 inch/sec at 1000 psi with a constant pressure slope of 0.7 up to 8000 psi. The fact their burn rates are so similar indicates that the faster burning ingredient (ADN) dictates the general overall burn rates of the propellant.

During formulation of the first series of CL-20/ADN minimum-signature propellants, three propellant binders were evaluated—ORP-2A/BTTN/TMETN, GAP/BTTN/ TMETN, and PCP/BTTN/TMETN. All

have shown to be excellent binders. The safety properties of the ADN/CL-20 propellants were measured and compared with the properties obtained with the ADN propellants (Table I). The propellant formulations exhibited better safety properties than the neat solids and were well within the safety limits of routine processing. In addition, the investigators observed that the ADN/CL-20 propellants were less impact sensitive than the ADN propellants.

Table I Safety Properties of Propellants

Propellant sample	Impact (2.5Kg,50%,cm)	ABL Friction (50%, lbs)	Electrostatic (0.25j)
PCP/NE/CL-20/ADN(75%)	16	631	10/10NF
OPR/NE/CL-20/ADN(75%)	16	769	10/10NF
ORP/NE/ADN(60%)	10	759	10/10NF
GAP/NE/ADN(60%)	9	501	10/10NF
Neat solid			
ADN	8-10	324-400	10/10NF
CL-20	9-10	200-300	10/10NF
RDX	17-20	500-660	10/10NF

NE= nitrate ester plasticizer

When the thermal properties of these formulations were evaluated, most of the samples exhibited an onset temperature around 157 to 161°C—the same temperatures at which ADN starts decomposing. The peak exotherms were around 172 and 222°C. The exotherms at 172 and 222°C represent the decomposition peaks of ADN and CL-20, respectively. The results from the VTS test were in the range of 0.1 to 0.2 cm^3/g/48 hr at 80°C, as shown in Table II. Because no early onset or synergistic reactions were detected, these results indicate that the materials are thermochemically compatible.

Table II. Thermal Properties of Propellants

Propellant sample	DSC/TGA, °C Onset, exotherm	VTS,80 °C cm^3/g/48 hr
PCP/NE/CL-20/ADN(75%)	157, 172 and 218	0.1
ORP/NE/CL-20/ADN(75%)	154, 177 and 222	0.1
ORP/NE/ADN(60%)	154, 170	0.2
Neat solid		
ADN	157, 187	0.2
CL-20	241, 257	0.01

The propellant samples contained 0.525% MNA as the thermal stabilizer. The neat ADN was about 50 micron in particle size and was purchased from Bofors in Sweden. Propellant samples (about 100 grams) were prepared for burn rate evaluation in the window bomb apparatus. The results showed that CL-20/ADN propellant can sustain good burn rates at various pressures. ADN/CL-20 propellants have a burn rate around 0.6-0.7 in/sec at 1000 psi and the ADN propellant exhibit similar burn rates. However, it tends to be sensitive to pressure variations—a condition that translates to a high pressure slope. The high pressure slope appears to be more of a CL-20 problem than that of ADN because propellant containing CL-20/ADN exhibited a higher slope (0.66 to 0.75) than the propellant samples composed of an ADN-only oxidizer (0.43 to 0.54).

Additional attributes of the final ADN and ADN/CL-20 formulations include: low shock sensitivity (less tham 70 cards in the NOL card gap test), good processing properties and no pressure slope breaks were observed up to 8K psi, thus these propellants have the potential of high pressure operation for higher performance. Other details can be found in the papers cited under the Publications section.

For the HCl-free UFAL task China Lake originally used CSD prilled ADN, but later ended up using crash-recrystallized ADN. Although the prills processed somewhat better, the crystalline material apparently imparted less sensitivity to the formulations. Photomicrographs of the prilled ADN showed many finely-broken fragments in a field generally composed of whole prills. When these samples were washed in dichloromethane, most of the whole prills broke into partial spheres. Analysis showed an extractable portion of 0.07%, probably the mineral oil used in the prilling process. It may be that the ADN prills break up on storage. This might explain the observation that formulations with the prilled material were originally less sensitive to friction and impact than crystalline material, but are more sensitive now.   FEM-ground prills were found to be badly caked and heavily contaminated with methanol-insoluble material, including grit particles and what appeared to be short hairs or brush bristles. Methanol solutions of this material were a deeper yellow color than solutions of prilled or crystalline material.   This may also explain the increased sensitivity of this pulverized material over the recrystallized ADN. Mixes containing ADN cure if the ADN is stored over sodium hydroxide under vacuum for 2 days.

Alane-precipitated aluminum (NAWCWPNS) gave problems with cures, and an alternate supply of supposed nano-grade aluminum from Nanomaterials research was mostly 10μ and larger and showed only 5% or so truly "nano" material, despite the high surface area claimed. We decided to cease the work with this material.

Efforts were made to scale up the mixes made with Argonide nanoaluminum. Mixes were made for strand burns: one a 500 gm repeat of the earlier windowbomb sample, which had a slope of 0.56 between 4000-6000 psi, and two more, at 150 gm, with and without BTATZ, a high-nitrogen material which burns rapidly with high energy and a low slope. BTATZ (*bis*-(aminotetrazolyl)tetrazine) (BTATZ) was synthesized by Dr. Michael Hiskey at Los Alamos National Laboratories, and is rare in being an energetic material which burns with a very low slope (0.2). We hoped that this material would impart the same qualities to our propellant formulations. The addition of 10% BTATZ (without any other slope reducing materials such as fumed alumina) to the formulation lowered the overall slope of the mixture from 0.74 to 0.57 over the entire range from 500-10000psi. The curve shows the slope is probably acceptable out to 6500-7000 psi. BTATZ at 5% levels did not have this effect on the slope. This formulation appears fully acceptable for further development.

Another method of curing propellant binders by reacting azide linkages with ethynyl groups to form triazoles has met with some success. This cure mechanism appears to be unaffected by materials which impede or halt urethane cures, such as certain alane-precipitated or plasma-process nanoaluminum preparations. We made an analogue of the formulation above using BAMO-NMMO and a diacetylene in place of PAO 24-13 and N-100.

This mixture was blended and cast at room temperature and cured at 120°F. Shore A hardness was 59 at 7 days. Strand burns gave calculated rates of 3.09-5.1 in/sec over the 4500-8000 psi range.

The overall slope is 0.754, with a slope break at 2000 psi, with n below this pressure on the order of 0.5. This mixture imparts a 3 sec Isp increase over the baseline formulation. Mechanical properties are fairly poor at present and additional work would be required to solve these problems.

We acknowledge the support by Dr's Hawkins and Ismail of Philip's Lab in the characterization of the aluminum powders used in these formulations.
Other details can be found in the papers cited under the Publications section.

Conclusions

Based upon the obtained results we conclude that viable lead- and HCl-free propellant formulations can be prepared, which actually can result in preformance increases over that of base-line propellants. Despite the fact that these results were obtained using "experimental" ingredients, a number of companies including Bofors (ADN), CSD (ADN) and Thiokol (CL-20) are gearing up for significant commercial production of these materials. The attractiveness of these formulations is based not only upon their "clean" attributes, but also their probable increased performance as well as the possibility of reduced hazards properties. Exhaust products like hydrochloric acid, chlorine and heavy metals have been completely eliminated. Predicted performance has been calculated to significantly exceed baseline current materials and the reduction of hazards might allow the production of 6.3 propellants with the performance of current 6.1 materials.

Summary

Two new high energy formulations using ADN and ADN/CL-20 are being studied. These formulations have 15% higher calculated performance than conventional minimum signature propellants. The new formulations also exhibit good safety, thermal and combustion properties. The formulations contain no lead or other heavy metals and the combustion products are basically benign gases with no HCl. The formulations appear to be real viable compositions and will be the subject of continued advanced deveopment under other programs (see Transitions). A UFAL formulation also appears to be promising for transition to other programs.

Transition Plan

Potential transitions range from possibilities to actual current efforts. Included in the possibilities are: Hellfire's expressed interest in lead-free CL-20 propellant technology and interest by the SPIKE program (proposed Marine man-portable smart weapon). There are presently efforts on ADN propellant manufacturing technology which are supported by the IHPRPT program (Integrated High Payoff Rocket Propulsion Technology). A Navy funded Insensitive Munition Technology Transition Program (IMTTP) is currently evaluating a version of lead-free CL-20 propellant for the 2.75 rocket. All of the apparently viable formulations developed under this SERDP program will continue to be marketed.

Publications

"Toxicity Review of Proposed Green Missile Components" by H.T. Bausum, and M.A. Major. May 1999 USACHPPM Project No. 87-9100-99

"Minimum Signature Propellant with a Mixed Oxidizer Concept" by May L. Chan and Alan Turner, published in the proceedings of NATO/RTA (Research and Technology Agency) conference on "Small Rocket Motors and Gas Generators for Land, Sea and Air Launched Weapons" April 19-23, 1999. Corfu, Greece.

"Physical and Chemical Characterization of Ultrafine Aluminum Powders" by Dr. Ismail Ismail and Dr. Tom Hawkins.1999 Pacific Conference on Chemistry and Spectroscopy (35th American Chemical Society Western Regional Meeting and 37th SAS Pacific Conference)

"ADN Technology Applied to Minimum Signature Propellants"
by May L. Chan Presented at the U.S./Sweden DEA SW-N-96-1505 meeting, Stockholm, Sweden, June 14-16, 1999.

 "Minimum Signature Propellants Containing No Lead Catalysts" by May Chan and Alan Turner. 1998 JANNAF Propellant Development and Characterization Subcommitee (PDCS) and Safety and Environmental Protection Subcommittee (SEPS) Meeting. April 21 - 23, 1998.

"ADN Propellant Technology" published in the Proceedings of Swedish DEA, a technical data exchange agreement meeting with the Defense Research Establishment of Sweden. January 20 - 23, 1998.

"The Green Missile Program: by Diane Hagler and Pam Carpenter. Keynote address at 1997 JANNAF Safety and Environmental Protection Subcommittee and Propellant Development and Characterization Subcommittee Meetings. March 17 - 20, 1997.

"Disposable Propellant Compositions Producing No Hydrogen Chloride", Reed, Ciaramitaro
JANNAF PCDS-S&EPS Meeting, April 1998 (CPIA Publication 674)

"Triazole Linkages as a route to More Robust Binder Cures", Reed, Ciaramitaro
JANNAF PCDS-S&EPS Meeting, December, 1999 (In Press)

Air Force Research Laboratory, Propulsion Directorate, Edwards AFB

Develop Complete and Clean, HCl-Free, Combustion of Propellant
(support to NSWC)

Technical Approach

Tactical and strategic boost motors utilize aluminum as a fuel to achieve the high performance required for their respective missions. It is well known that chlorinated oxidizers such as ammonium perchlorate (AP) are employed to effectively combust aluminum fuel. Non-halogenated oxidizers like ammonium nitrate (AN) have often fallen short of achieving efficient aluminum combustion due to difficulty in obtaining sufficiently high combustion temperatures to overcome the character of the aluminum oxide on the surface of the fuel. Ultrafine aluminum (UFAL) fuel is under investigation as an avenue to provide more efficient combustion of aluminum and improved ballistic properties with environmentally beneficial, non-halogenated oxidizers.

The Air Force Research Laboratory (AFRL) task in the Green Missile program is to support the development of environmentally enhanced, high performance solid propellant through characterization and evaluation of new UFAL fuels and selected advanced propellant formulations incorporating UFAL. The suitability of UFAL fuels will be evaluated for use in an environmentally enhanced solid, space booster propellant that incorporates a nonhalogenated oxidizer such as ammonium nitrate.

The Air Force approach to accomplish the Green Missile task draws from experience with fine aluminum fuel technology. Air Force funded work in fine aluminum powder production and evaluation in the early 1970's by Atlantic Research Corporation[1]. The project produced this material using helium or argon plasma to vaporize aluminum metal, followed by precipitation in a jacketed copper condensation tube. Small quantities (approximately 10 grams were produced in a single batch run) were examined and a limited amount of solid propellant produced with these powders. The average particle diameters of the powders were measured and all were reported as being greater than 200 nm with many being in the range of 500-1000 nm. Enhanced burning rates were observed with AP-based propellants incorporating these powders versus standard aluminum fuel. These results presaged more recent research on the ignition and combustion of aluminum particles at high temperature (2630 K) and pressure (37 – 140 atm) such as that by Foelsche et al.[2] The combustion time of the metal particles have been found to correlate with their diameter in a manner that predicts complete combustion of 100 nm aluminum particles in approximately 1 μs as depicted in Figure 1.[2,3] Such fast burn times lead to a possibility of improved energy feedback of metal particulate combustion to the propellant surface to permit enhanced propellant burning rate.
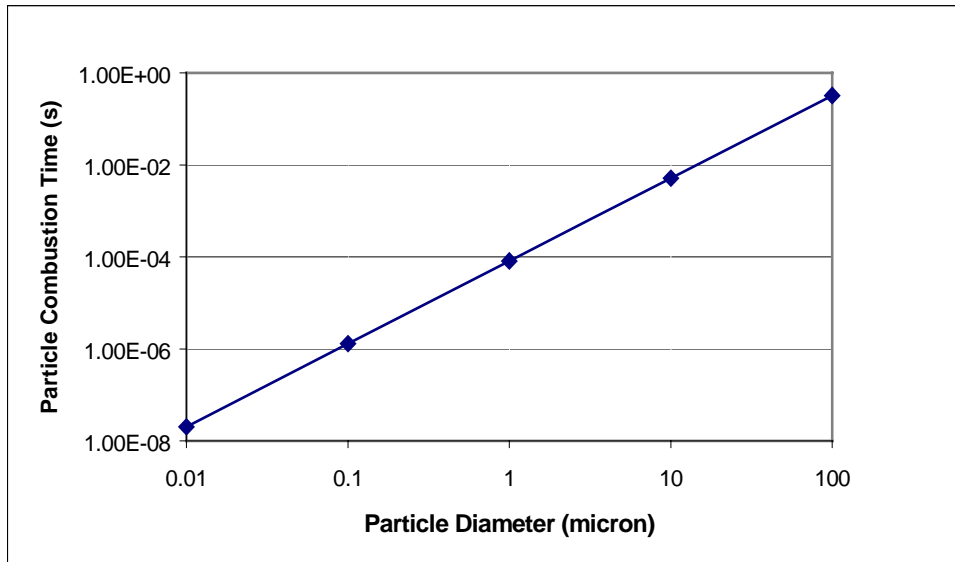
Figure 1   Correlation of Particle Combustion Time with Particle Diameter

The WFZ propellant shown in Table 1 was selected as the baseline.

Table 1. WFZ-Propellant- General Composition

COMPOUND	CONCENTRATION (WT%)
POLYETHER PREPOLYMER (TPEG)	5.45
N-BUTYL 2-NITRATOETHYL NITRAMINE (BUNENA)	7.70
TRIMETHYLOLETHANETRINITRATE (TMETN)	7.19
CURATIVE (DESMODUR N100)	1.03
CURE CATALYST (TEPB)	0.04
AMMONIUM NITRATE (40 μm)	10.0
AMMONIUM NITRATE (200 μm)	45.0
MG-AL ALLOY (50/50) POWDER	23.0
BONDING AGENT/PROCESS AID (DER 331/TET)	0.10
STABILIZER (MNA/2-NDPA)	0.49

While the WFZ propellant has some very attractive qualities, it possesses a volumetric impulse that was lower than that of propellant in fielded systems such as Delta II GEM or Titan IV SRMU. Consequently it is desirable to maintain the specific impulse, safety/sensitivity and ballistic characteristics, while increasing the volumetric impulse. It was apparent that the introduction of ultrafine aluminum (in this case ALEX) in place of a portion of the magnesium-aluminum alloy could certainly improve the density of the resulting propellant. A comparison of the density of aluminum (2.7 g/cc) with that of the magnesium-aluminum alloy (2.2 g/cc) makes this obvious. However, it was recognized that the oxide coating (approximately 10 % by wt.) of the UFAL acts as inert mass and detracts from the specific impulse.[5,6] After some trade calculation, it was found that the loss in impulse from the inert oxide coating

was largely offset by the gain in impulse from using aluminum metal in place of the magnesium-aluminum alloy. (Significantly higher exothermicity of aluminum combustion drives the chamber temperature higher than that obtained from the alloy.) In addition, the use of a submicron-sized fuel brings potential of a reduction in two-phase flow losses and potential improvement in propellant combustion efficiency.

It could not be determined with certainty whether the combustion environment surrounding the UFAL particles of the AN-based propellant would have sufficient reaction chemistry to drive their combustion. Also, simulation and modeling technology does not exist to render an *a priori* determination of the effect UFAL on the safety/sensitivity properties of the propellant. Thus the modification of the WFZ propellant with UFAL (i.e., ALEX) has been undertaken in an attempt to assess the impacts of such modification. This report has particular emphasis on the effects of UFAL addition on propellant combustion and ballistics determined from strand-burner and 2x4 motor tests. Safety and sensitivity test results from UFAL-modified propellant are also addressed.

The Environmental Protection Agency performed a study entitled "The Pollution Prevention Potential of the Green
Missile Program." This study examined the effects of the AFRL developed propellant on the environment and is being published separately from this report.

Accomplishments And Results

The following accomplishments may be claimed by this work,

1. Straightforward substitution of UFAL for Mg-Al alloy in an environmentally enhanced, booster propellant can incrementally improve its volumetric impulse.

2. Good propellant processability is achievable with formulations of relatively high concentration (up to 18 wt%) of UFAL.

3. Furthermore, the use of UFAL provided discernible benefits to the ballistic properties of the ammonium nitrate-based propellant- particularly if a low concentration of UFAP is used as a ballistic modifier.

4. Test results demonstrate that UFAL-containing propellant is a zero-card, Class 1.3 propellant.

5. Also a candidate, UFAL-based propellant was successfully scaled to the 1 gallon mix-level and a series of (2x4) ballistic test motors produced and tested. The UFAL-containing propellant exhibited a regression rate that closely matches that of a space-launch booster propellant and has a slightly higher (but not unreasonably high) exponent in its burn rate-pressure curve.

PROPELLANT DEVELOPMENT AND CHARACTERIZATION
SMALL-SCALE FORMULATION AND CHARACTERIZATION
EXPERIMENTAL
Materials/Compounds:
1) Ammonium Nitrate (AN) - Laurylamine-coated AN obtained from Laroche
2) Ultrafine Aluminum (UFAL) - UFAL was obtained from Argonide Corporation as ALEX^{TM}.
3) Polyether (TPEG) - TPEG was obtained from Pressure Chemical Inc. (Block Copolymer , M.W. =3000)
4) N-butyl 2-nitatoethyl nitramine (BuNENA) – RXL 647 Stabilized BuNENA was obtained from NSWC-Indian Head

5) Trimethylolethanetrinitrate (TMETN) – TMETN was obtained from Rocketdyne Corporation
6) Mg/Al (50/50) Alloy – Atomized spherical Mg/Al was obtained from Valimet Corporation
7) Dow Epoxy Resin (DER 331) – DER 331 was obtained from Dow Chemical Corporation
8) Triethoxyphenyl bismuth (TEPB) – TEPB was obtained from Boulder Scientific Company
9) N-methyl p-nitroaniline (MNA) – MNA was obtained from American Cyanamide
10) 2- nitro diphenylamine (2-NDPA) – 2-NDPA was obtained from Aldrich Chemical Company
11) Triethylenetetramine (TET) – TET was obtained form Mallinkrodt Corporation
12) Desmodur N-100 – N-100 was obtained from Miles Inc.
13) Ammonium Perchlorate (AP) – AP (200 μm) was obtained from WECCO
14) Ultrafine Ammonium Perchlorate (UFAP) – UFAP (0.50 μm) was obtained from Aerojet Solid Propulsion Company

Propellant Formulation
Propellants were typically produced at ¼-1 pint-scale employing a vertical, Ross-type, planetary mixer. Vacuum was applied during propellant processing to reduce voids. The propellants were cured at 120° F for 5 days.

Propellant Test and Evaluation
Detonability testing was performed according to standard NOL Card Gap methodology. Friction sensitivity testing was performed with a Julius Peters Model 21 instrument, and an Olin Mathieson Model 7 drop weight tester was used to determine impact sensitivity of propellant samples. The ballistic characterization of propellant samples (propellant strands) was accomplished in a strand-burner apparatus capable of operating at pressures near 2000 psi.

DISCUSSION
Effect of UFAL Addition
A trade study was first performed with a WFZ-type propellant to determine the effect of UFAL addition on volumetric impulse. The volumetric impulse was calculated using USAF ISP software, and both metal fuels (UFAL and Mg-Al alloy) were incrementally placed into a WFZ matrix (sans metal fuel) as outlined in Table 1. An accounting for the aluminum oxide content of the UFAL (in this case ALEX^{TM}) was considered in the calculations. The results of the computations are seen in Figure 2. One observes a decidedly larger volumetric impulse from the UFAL versus the alloy. This trend is the desired direction for performance improvement for the booster propellant.

Ballistic characteristics were obtained via strand burner for a series of propellant formulations incorporating varying concentrations of UFAL. The formulations were based on the WFZ composition with total metal (i.e., Mg-Al alloy plus UFAL) concentration held constant at 23 wt%. All formulations displayed low end-of-mix viscosities (< 3 kP) and the cured propellants had acceptable impact sensitivities (> 70 kg∗cm). The results of the ballistic evaluation over a pressure range of 500–1500 psi are displayed in Figure 3. The results show the regression rate is generally lowered as the concentration of UFAL is increased. This finding can be interpreted to indicate that the combustion chemistry and temperature necessary for efficient UFAL combustion at the burning propellant surface are not being achieved for the formulation. This finding may not be surprising if the UFAL is viewed as not possessing any discernibly different properties from commercial aluminum fuels. However, as stated in the TECHNICAL APPROACH, UFAL does exhibit differences in combustion behavior from these commercial fuels.
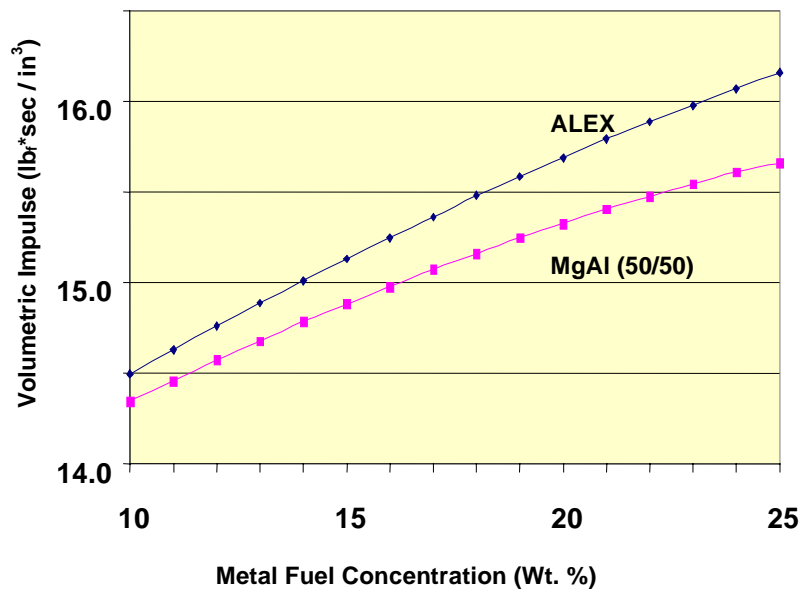
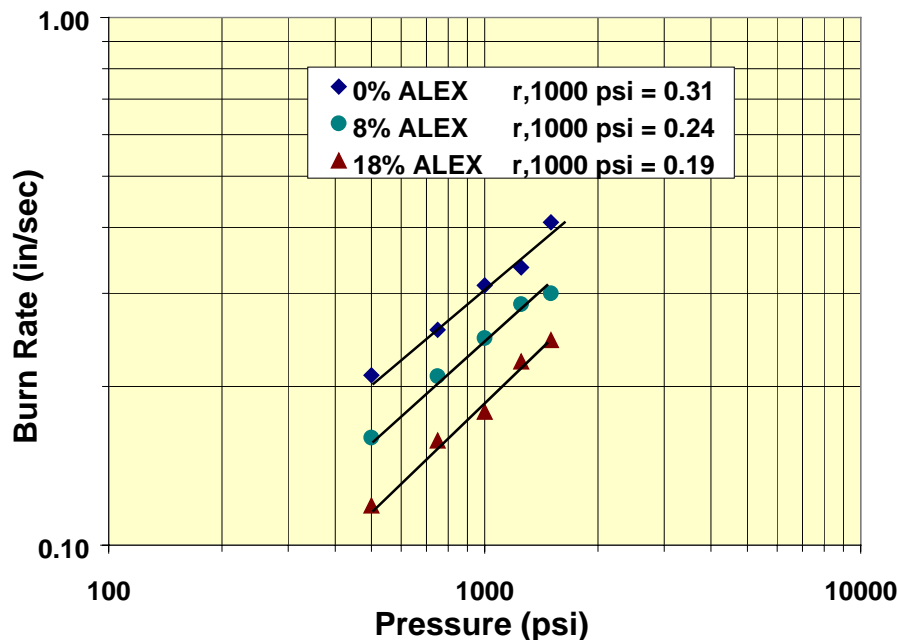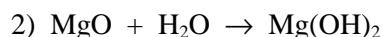**Figure 2   Effect Of Metal Fuels on Volumetric Impulse**

Figure 3   Ballistic Property Evaluation of UFAL Addition to WFZ-Type Propellant With Total Metal Fuel Content (Mg-Al + UFAL) at 23 wt%

Effect of AP Addition

The results from Figure 3 made it clear that modification of the propellant composition was necessary to improve the combustion and ballistic properties of UFAL-containing propellant. Past work with AN-based propellants has shown that the addition of ammonium perchlorate at relatively low levels can have a beneficial effect on ballistic properties.[7] Also, it was recognized that the addition of a small quantity of ammonium perchlorate introduces a potential for a correspondingly small quantity of hydrochloric acid in the exhaust of a motor using the propellant. Theoretical calculation indicates a propellant incorporating

WFZ-binder, 18% UFAL, 5% Mg-Al alloy, 50% ammonium nitrate with 5% ammonium perchlorate would emit 1.5% hydrochloric acid in the exhaust. Furthermore, a neutralization reaction (that is known to occur within the exhaust between hydrated magnesium oxide and hydrochloric acid) would act to potentially diminish this exhaust acid content to an insignificant level. The neutralization reaction sequence is shown below,

1) $Mg + NH_4ClO_4 \rightarrow MgO\ +\ HCl\ +\ MgCl_2$ $[HCl] \gg [MgCl_2]$

2) $MgO\ +\ H_2O\ \rightarrow\ Mg(OH)_2$

3) $Mg(OH)_2\ +\ 2HCl\ \rightarrow MgCl_2\ +\ 2H_2O$

Consequently, two such propellant formulations were produced – one formulation containing 5% ammonium perchlorate (200 micron particle size) and the other formulation containing 5% ultrafine ammonium perchlorate (0.5 micron particle size). Both formulations displayed satisfactory end-of-mix viscosities and, after cure, exhibited acceptable impact sensitivities (> 70 kg*cm). Also, detonability testing of the UFAP-containing propellant showed it was a zero-card, Class 1.3 propellant. The ballistic properties of the propellants were compared to a control propellant employing no ammonium perchlorate. The results are shown in Figure 4 and indicate the ability of the UFAP to increase regression rate to a much higher degree than the coarser AP. The ability of UFAP to enhance regression rate has been previously noted and explored in research dating to the 1970's with AP-based propellants.[8]

Effect of Aluminum Fuel Size on Propellant Ballistics
Having established the accessibility of acceptable ballistic properties with an UFAL-containing propellant modified with a small amount of UFAP, a natural question arises regarding the need for UFAL compared to a commercial aluminum fuel of larger particle size. Consequently, a formulation containing MDX-65 (with aluminum particle size near 6 µm) was produced and compared to the corresponding formulation made with UFAL. The ballistic behaviors of the two propellants are depicted in Figure 5. It is apparent that the UFAL makes a distinct and beneficial contribution to the propellant ballistic characteristics. In addition to significantly improving regression rate, the exponent is reduced with use of UFAL.

Regression rates (measured at 1000 psi) typically lie between 0.26 to 0.32 inch/s, and burn-rate exponents typically fall between 0.3 to 0.4 for currently fielded space-launch boosters. The UFAL-containing propellant in Figure 5 has exhibited a regression rate that closely matches that of a space-launch booster propellant and has a higher (but not unreasonably high) exponent.
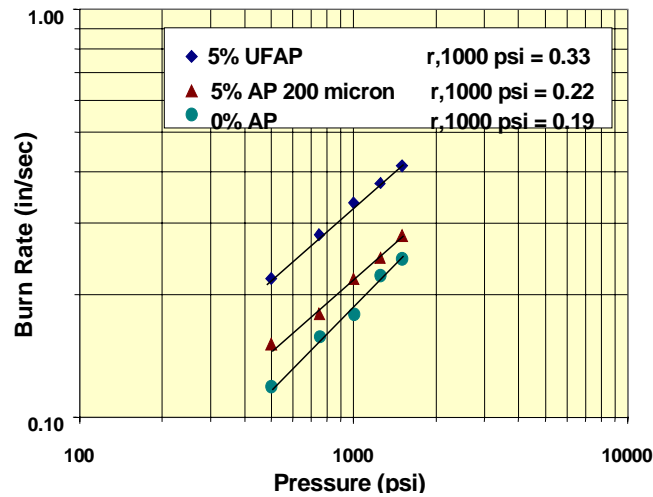
Figure 4   **Effect of Ammonium Perchlorate Addition on Ballistics of Propellant with 18 wt% UFAL, 5 wt% Mg-Al Alloy and 55 wt% Oxidizer (AN + AP)**
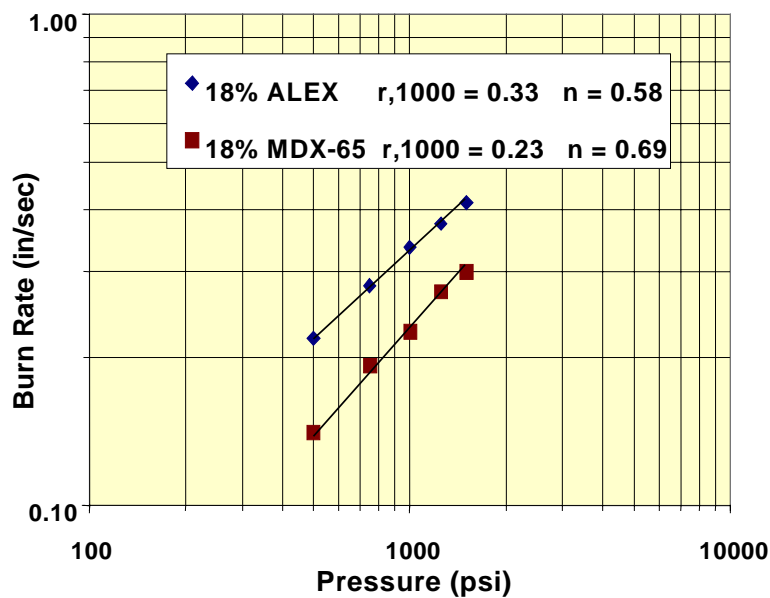

Figure 5   **Effect of Type of Aluminum Fuel on Ballistics of Propellant with 18 wt% AL, 5 wt% Mg-Al Alloy, 5 wt% UFAP and 55 wt% Oxidizer (AN + AP)**

In terms of performance, the use of UFAL and a small concentration of ballistic modifier in the form of UFAP does improve volumetric impulse of the point-of-departure WFZ-type propellant produced by Alliant Techsystems in the USAF Clean Propellant Development and Demonstration program. Many fielded booster propellants have standard specific impulse that ranges between 261 to 264 lb_f s/lb_m, and possess standard volumetric impulse that lies between 16.7 to 17.1 lb_f s/in^3. The UFAL-containing propellant has a standard specific impulse near 260 lb_f s/lb_m, and a standard volumetric impulse at 16.0. At this point in its development, the propellant displays respectable performance attributes for an environmentally enhanced booster propellant.

PROPELLANT SCALE-UP AND MOTOR FIRING
Subsequent to the SMALL-SCALE FORMULATION AND CHARACTERIZATION TASK a propellant candidate was downselected for formulation scale-up and test-firing in a series if 2x4 motors. The propellant formulation incorporated ammonium nitrate oxidizer (50 wt%), polyether binder with high-energy plasticizer, magnesium-aluminum alloy fuel (5wt%), ALEX (18 wt%) and a low level (5 wt%) of combustion modifier (ultrafine ammonium perchlorate). It was theoretically calculated to possess standard specific impulse between 259 to 260 $lb_f$$s/lb_m$. The baseline propellant (WFZ) was also placed into a series of 2x4 motors for use as a control. A description of the effects of UFAL addition on propellant ballistics determined from these motor tests follows.

EXPERIMENTAL
Propellant Formulation
Propellants were produced at the one-gallon scale with a vertical, Ross-type, planetary mixer. Vacuum was applied during propellant processing to reduce voids. The propellants were cured at 120° F for 5 days.

Propellant Test and Evaluation
A series of 2x4 (ca. 100 gram-scale) motors were prepared that incorporated the downselected propellant and a separate motor series prepared with the WFZ propellant. These motors were center-perforated grains with a 0.25-inch web thickness. The test firings were conducted at the AFRL facility at Edwards AFB CA.

TECHNICAL DISCUSSION
The ballistic behavior of WFZ propellant is shown in Figure 6. The burn rate exponent of 0.52 and the burn rate of 0.289 in/s at 1000 psi chamber pressure are very similar to the motor data reported by Alliant Techsystems in the previous Clean Propellant Development and Demonstration Program sponsored by USAF. Also this motor data supports the combustion window bomb and strand-burning test results obtained in this program (in the SMALL-SCALE FORMULATION AND CHARACTERIZATION TASK).
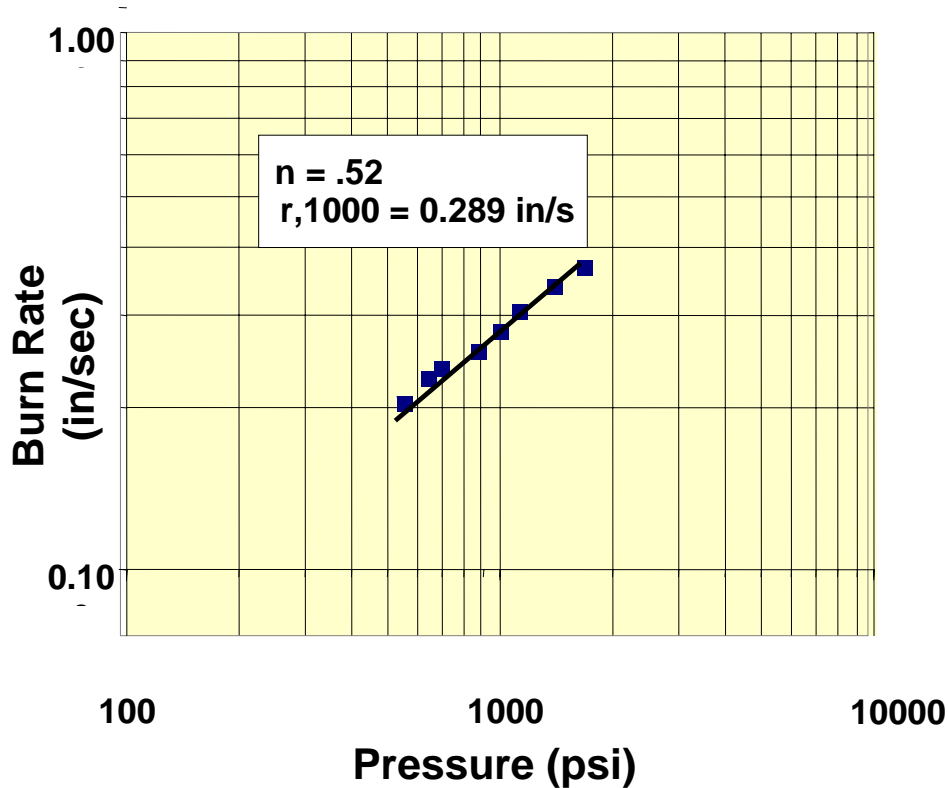
Figure 6   Burn rate behavior of WFZ propellant as a function of 2x4 motor chamber pressure

The motor ballistic behavior of the UFAL-containing propellant candidate is shown in Figure 7, and a typical test result (chamber pressure versus time curve) for a motor firing is displayed in Figure 8. This propellant was comprised of a WFZ-based binder system with 18 wt% UFAL, 5 wt% Mg-Al alloy and 50 wt% ammonium nitrate with 5 wt% ballistic modifier (ultrafine ammonium perchlorate). The burn rate exponent of 0.53 and the burn rate of 0.305 in/s at 1000 psi chamber pressure are very similar to the motor data from the WFZ control propellant. Moreover, the burn rate is actually higher than the control propellant and this is a significant improvement over the baseline WFZ propellant. Motor ignition delay was minimal (ref. Figure 8) with good, neutral behavior of the motor pressure.
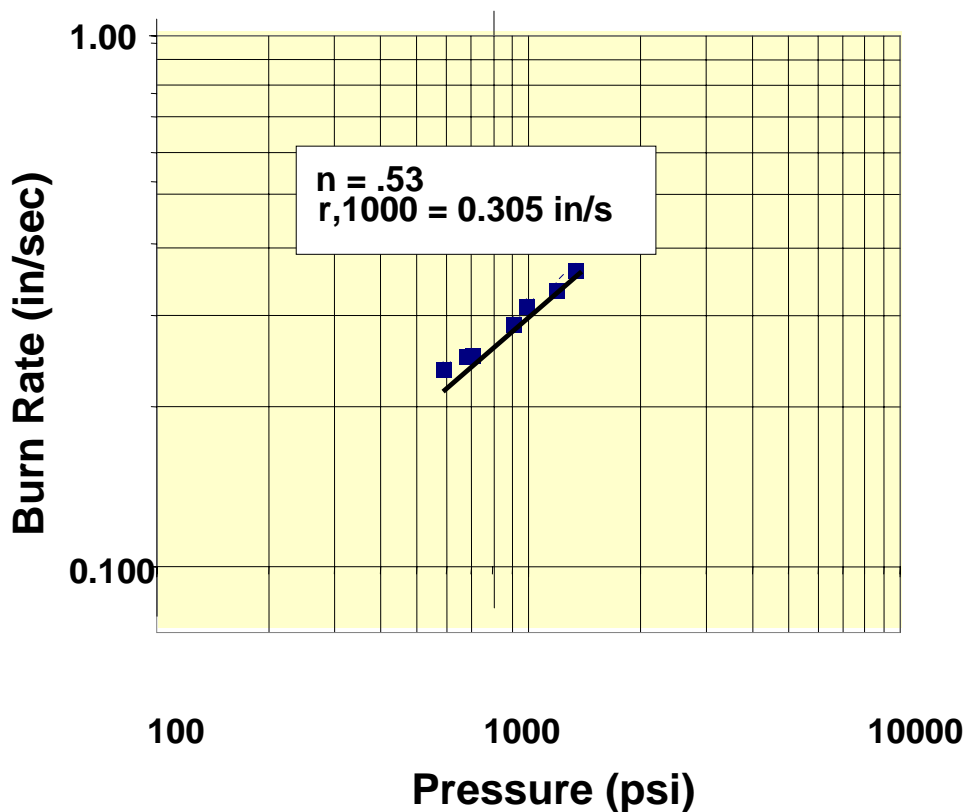
Figure 7   **Ballistic Property Evaluation of UFAL-Based Propellant With Total Metal Fuel Content (Mg-Al + UFAL) at 23 wt%**

Regression rates (measured at 1000 psi) typically lie between 0.26 to 0.32 inch/s, and burn-rate exponents typically fall between 0.3 to 0.4 for currently fielded space-launch boosters. The UFAL-containing propellant in Figure 7 has exhibited a regression rate that closely matches that of a space-launch booster propellant and has a higher (but not unreasonably high) exponent.

In terms of performance, the use of UFAL and a small concentration of ballistic modifier in the form of UFAP does improve volumetric impulse of the point-of-departure WFZ-type propellant produced by Alliant Techsystems in the USAF Clean Propellant Development and Demonstration program. Many fielded booster propellants have standard specific impulse that ranges between 261 to 264 lb_f s/lb_m, and possess standard volumetric impulse that lies between 16.7 to 17.1 lb_f s/in^3. The UFAL-containing propellant has a standard specific impulse near 260 lb_f s/lb_m, and a standard volumetric impulse at 16.0. At this point in its development, the propellant displays respectable performance attributes for an environmentally enhanced booster propellant.
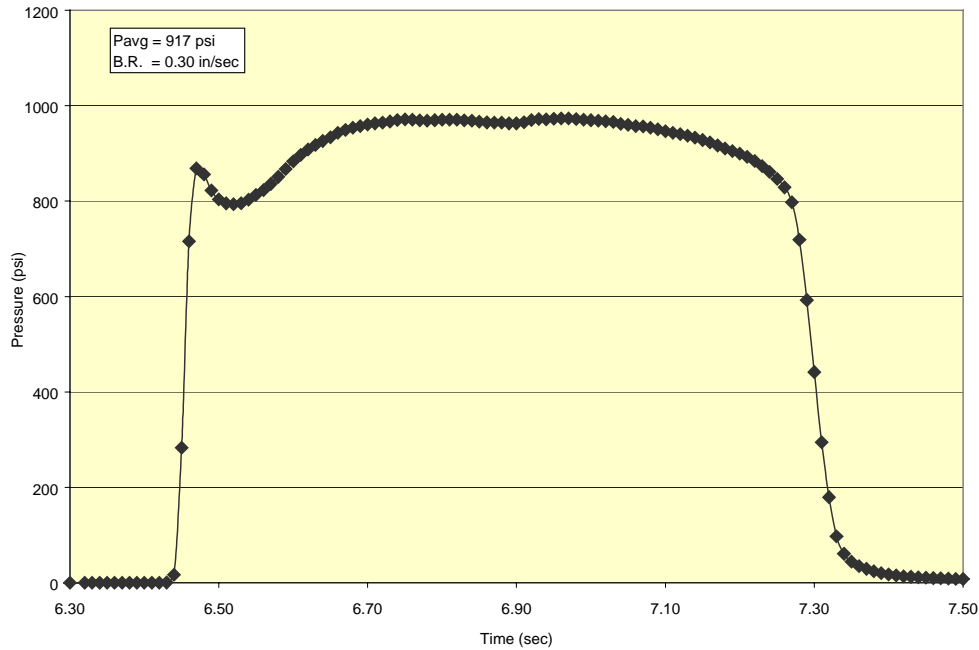
Figure 8   Chamber Pressure Versus Time Profile for 2x4 Motor Test of UFAL- Based Propellant Candidate

Conclusion

In conclusion, the main results of this propellant development task are as follows,

1. Theoretical evaluation of the straightforward substitution of UFAL for Mg-Al alloy in an environmentally enhanced, booster propellant showed improvement in volumetric impulse.

2. Good propellant processability was achieved with formulations of relatively high concentration (up to 18 wt%) of UFAL.

3. Determined that UFAL provided discernible benefits to the ballistic properties of the ammonium nitrate-based propellant- particularly if a low concentration of UFAP is used as a ballistic modifier.

4. Demonstrated that UFAL-containing propellant is a zero-card, Class 1.3 propellant.

5. Also a candidate, UFAL-based propellant was successfully scaled to the 1 gallon mix-level and a series of (2x4) ballistic test motors produced and tested. The UFAL-containing propellant exhibited a regression rate that closely matched that of a space-launch booster propellant and has a slightly higher (but not unreasonably high) exponent in its burn rate-pressure curve.

Summary

An environmentally enhanced solid propellant formulation has been developed that incorporates (and benefits from) UFAL fuel. This propellant exhibits excellent processability and safety characteristics while achieving good ballistic properties. The performance of the propellant is comparable to fielded, space-boost propellants that emit high levels of hydrochloric acid. This propellant development effort has achieved a TRL (technical readiness level) of 3 and requires additional programming to transition to a demonstration program (TRL = 5) that will provide performance data necessary for translation into operational systems.

Transition Plan

Based on the promising results of this program, AFRL believes the program should continue (possibly as an ESTCP program) to address the final issues needed to implement the propellant in a commercial (or military) booster motor. The demonstration of an environmentally enhanced booster motor of commercial scale would provide the propulsion industry with a significant alternative to present booster systems. This is particularly important if environmental regulation continues to pressure launch operations to minimize environmental impact.

Recommendations

Further work would have to focus on system trade studies to define effects of current propellant candidate on system (e.g. Titan or Delta) performance, scaleability of current propellant for larger motor tests, evaluation of combustion efficiency of current propellant candidate, development/characterization of effective motor liners and insulation, and a determination of the effect of the propellant combustion on motor components such as the motor nozzle.

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Develop Thermoplastic Elastomer Based Inhibitors

Technical Approach

The baseline for the 2.75 inch rocket motor propellant is a nitrocellulose/nitroglycerine-type propellant with Pb/Cu double salt ballistic modifier. The baseline system uses an ethyl cellulose tape-wrapped inhibitor that is sealed with acetone solvent. This inhibitor is not suitable for use with advanced TPE propellant since it does not bond to the propellant. The objective of this research was to develop Thermoplastic Elastomeric-based (TPE-based) grain inhibitors for the following NSWC-IH 2.75 inch rocket motor propellant candidates: (1) Hytrel-based TPE propellant; (2) poly-BAMO/AMMO-based TPE propellant, or suitable substitute; and (3) extruded composite propellant.

Three different polymeric inhibitor systems were evaluated as potential replacements for the baseline cellulosic inhibitor. These TPE-type systems are based on chemical structures, which were expected to confer the ability to adhere to the new TPE-propellant, protecting the high-reactive material from external stress. The candidates were polyphosphazenes, POSS-polyurethanes, and POSS-polynorbornylenes (POSS = polyhedral oligomeric silsesquioxane). The polyphosphazenes were synthetically made, however, with the limited budget of 50K/yr it was decided to focus on the POSS-polyurethanes and POSS-polynorbornylenes. The approach consisted of the development of these new monomers and polymers, thorough physical and mechanical characterization of the two materials, down-selection to one candidate, scale-up and small scale live-propellant firing at NSWC-IH where the propellant had been wrapped with the selected inhibitor.

Introduction of Polyhedral Oligomeric Silsesquioxanes (POSS): The development of an thermoplastic elastomeric (TPE) inhibitor is based on the use of Polyhedral Oligomeric Silsesquioxane (POSS) hybrid inorganic/organic materials. During the last nine years the Polymeric Materials Applications branch at AFRL has demonstrated how incorporating POSS nanotechnology imparts improved and multiple enhancements to polymers & materials. Numerous papers, reports and talks have been given detailing the inherent benefits of polymerizing or blending such silicon oxygen systems into organic and inorganic polymers. Advantages include increases in Tg, use temperature, Tdec, oxidation and flammibility resistance.[1] Air Force applications for POSS nanotechnology have been identified based on the physical property enhancements listed in Figure 1, and include uses in ablative, structural, optical, space resistant resins/coatings, and electronic materials. POSS-polymers are currently being designed for jet canopies, turbine engine lubricants, housing and ducting in liquid rocket engines, radomes and thermal insulation for rockets, and as low-density, space-survivable resins for space vehicle systems.

Background & History: The discovery of the self-condensation of alkyltrichlorosilanes ($RSiCl_3$) to yield structurally well-defined silicon oxygen frameworks has been credited to Brown and Vogt in the mid-sixties while working at GE.[2] Their published results describe the reaction of $CySiCl_3$ with H_2O in acetone to yield a mixture of Polyhedral Oligomeric Silsesquioxanes (POSS) over a three year incubation period (Scheme I).

Scheme I
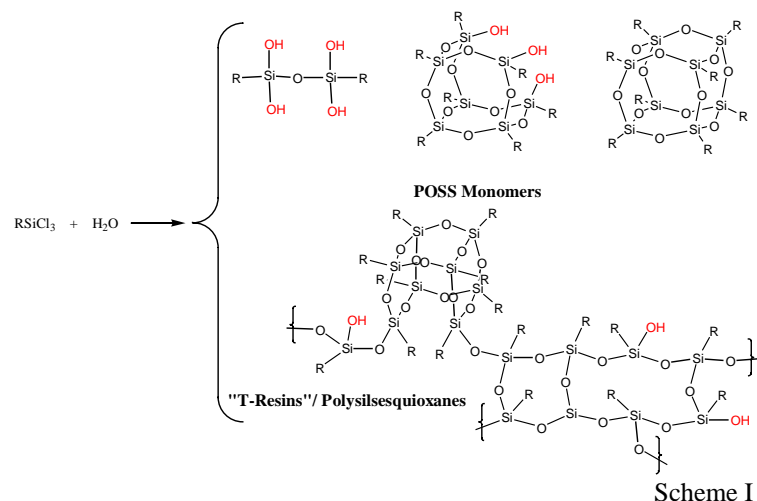
The first POSS polymer was a POSS-siloxane bead copolymer, which was tested for space applications (equation 1). This material exhibited incredible atomic oxygen and vacuum ultraviolet radiation resistance with a one hundred fold improvement in degradation resistance by forming a passive SiO_2 layer.[3] Early success stories helped create a rapidly expanding niche for new hybrid polymers containing POSS macromolecules.
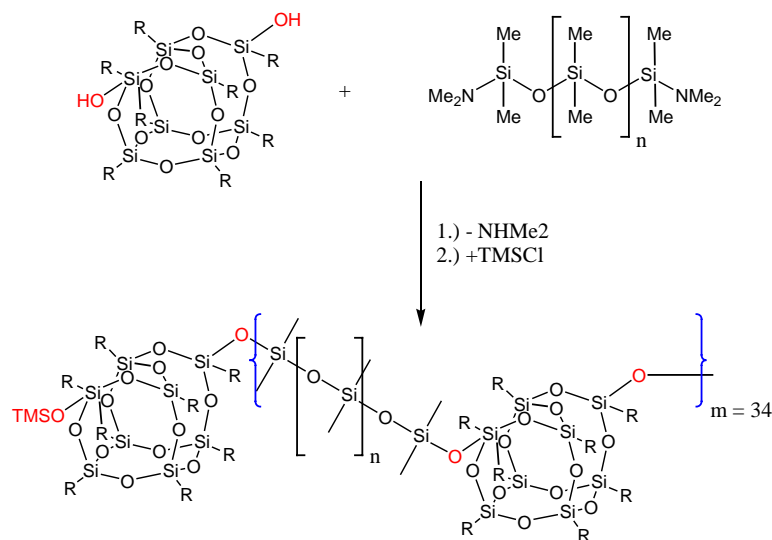
(1)

The success of POSS hybrid polymers is represented by the property enhancements outlined in Figure 1. Bead, Pendant, Triblock, and Dendrimeric POSS polymers have been made as homopolymers and copolymers. Also, blending of POSS monomers, polymers, and resins is readily achieved without drastically altering the processing conditions of the copolymer, an important footnote for manufacturing and/or commercialization.

46

Accomplishments

POSS-polyurethane polymers: Monomer and Polymer Synthesis: Two POSS-polyurethane monomers (Figure 1) were synthesized and fully characterized. Each involved the development of new synthetic methodologies, however, readily available starting materials were used.
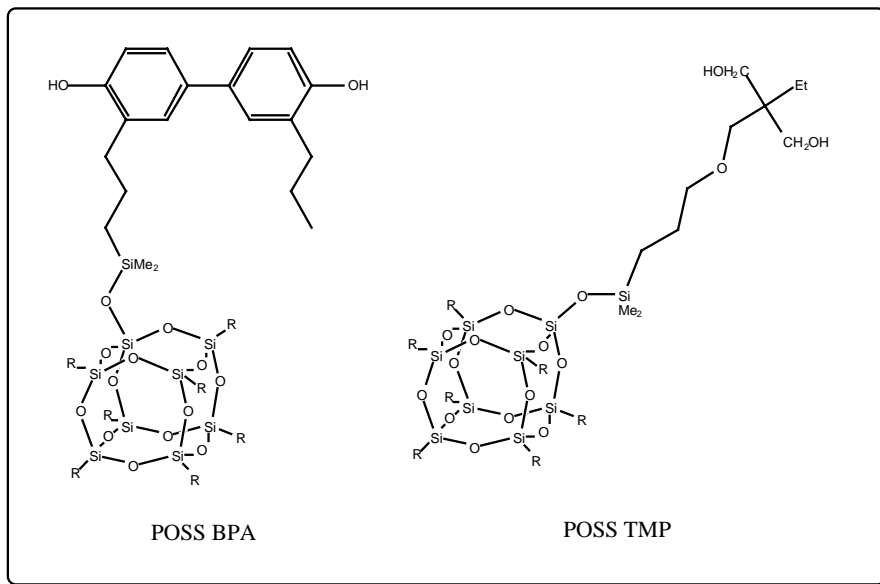

Figure 1   Two of the POSS monomers synthesized for urethane incorporation

POSS-polyurethanes were prepared using the well-published prepolymer method, involving the reaction of the POSS monomer with HMDI followed by addition of PTMG (Figure 2). The resulting polymers were isolated by precipitation into methanol. The POSS was incorporated into the hard segment of the polymer to increase the strength (moduli) of the TPE. POSS composition in the polymer was varied from 0 to 43 wt. % for each polymer.
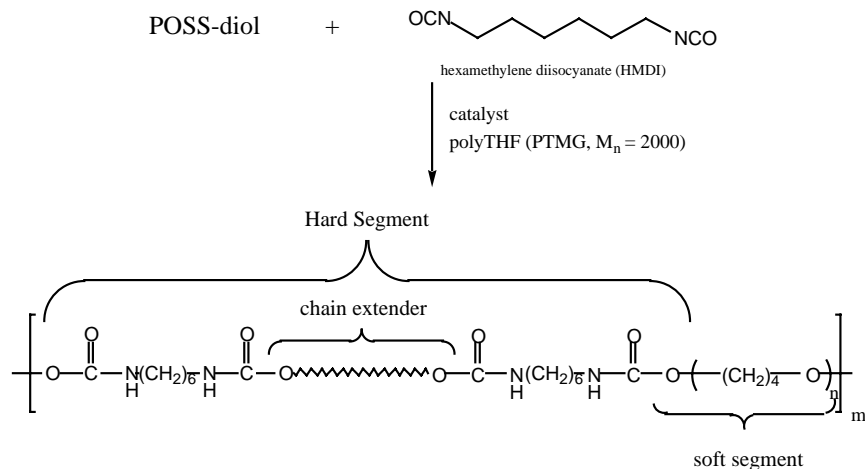

Figure 2   Synthesis and structure of polyurethane polymer using a prepolymer method.

Standard characterization techniques were implemented in order to insure/investigate the property enhancements of POSS incorporation. Rheological data for a 43 wt. % POSS-urethane polymer clearly shows the rubber behavior of the polymer. This data confirms that we do indeed still have a TPE, and the

POSS loading does not result in the formation of a brittle material. Stress-vs.-strain data of POSS containing urethanes show significant increases in the modulus and strength relative to the non-POSS urethanes. A ten-fold increase in modulus is observed with as little as 17 wt. % POSS. Over 400% elongation of the polymer is observed, and memory retention (ability to relax back to original size) was controllable. TGA data of the polymers show a slight increase in T_{dec}, furthermore POSS incorporation increased the char yield of the polymer.

	wt. % POSS	Modulus (MPa)	T_{dec} (°C)
POSS-TMP Urethanes	0	0.01	334
	17	0.14	344
	34	0.39	351
POSS-BPA Urethanes	0	0.04	317
	21	0.42	340
	36	1.06	352

The POSS-polyurethanes TPE Shore A hardness was significantly higher than without POSS, with up to a 180% increase. Important to note was that traditional filler technology does not result in increased hardness of the TPE. While these results showed promise, the processing of the materials was not easy. Normal polyurethane are difficult to extrude or press however, in many cases the addition of POSS can act as a flow-aid. For this particular polymer system it did not occur and the POSS-polynorbornylene polymer system, which were being developed at the same time, was chosen as the primary candidate.

POSS-polynorbornylene polymers: Monomer and Polymer Synthesis: Two POSS-polynorbornylene monomers were synthesized and fully characterized. The main difference in the monomers was the non-reactive organic group of each corner of the POSS framework. Surprisingly, a small change from R = cyclohexyl to cyclopentyl has a dramatic effect on not only the solubility of the monomer, but also the degree of property enhancement, as is evident from the polymer characterization data.The cyclochexylPOSS-polynorbornylene monomer has increased Tg and tensile moduli over the cyclopentylPOSS-polynorbornylene monomer. However unlike the cyclohexyl system, the cyclopentyl material is readily available, and property enhancements are significant enough for its use if large volumes are needed.

POSS-polynorbornylenes were prepared via a catalyzed Ring-Opening Metathesis Polymerization (ROMP) (Figure 3). From this reaction copolymers and homopolymers were made with varying wt. % of POSS incorporation. In addition, block or random copolymers were made, and it was determined that random copolymers resulted in the best property enhancements.
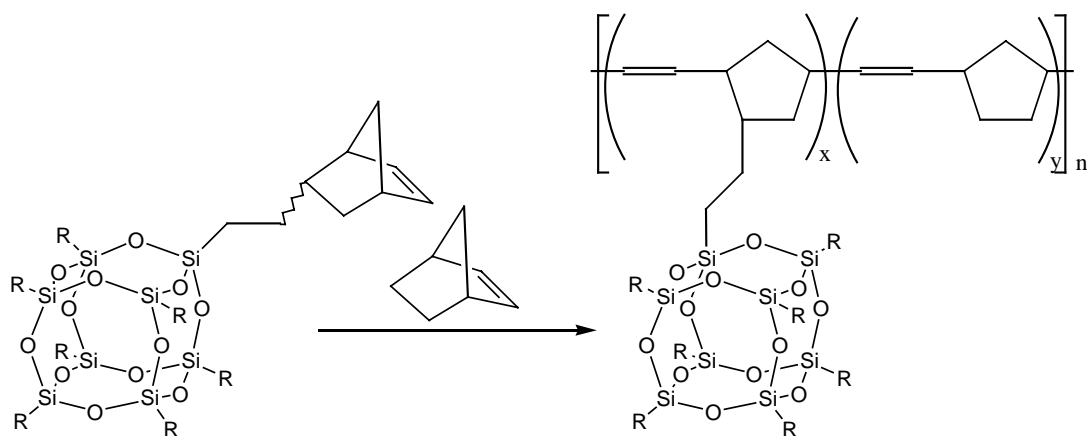
Figure 3 **Synthesis of POSS-polynorbornylene copolymers. Random copolymers were obtained via direct addition of POSS-polynorbornylene and polynorbornylene. Block copolymers were obtained via the stepwise addition of each monomer.**

As can be seen below, the initial moduli of the poly(polynorbornylene) and POSS-polynorbornylene TPE are very similar, and the maximum strain of the POSS-polynorbornylene TPE remains relatively high-in spite of the large POSS loading in the molecule. This is very encouraging since it indicates a relatively wide range of POSS concentrations are available for evaluation as restrictor coatings.

Tensile Property	wt. % POSS	Modulus (MPa)
Initial Modulus; Eo (MPa)	0	0.01
Maximum Strain; $_{max}$ (%)	17	0.14

Further DSC studies on the POSS-polynorbornylene polymers showed a significant T_g increase for the random copolymers, while the block copolymers showed almost no change in the T_g. The effect was more pronounced for the cyclohexyl system, where TEM data showed more intense POSS-POSS interactions than in the cyclopentyl system.
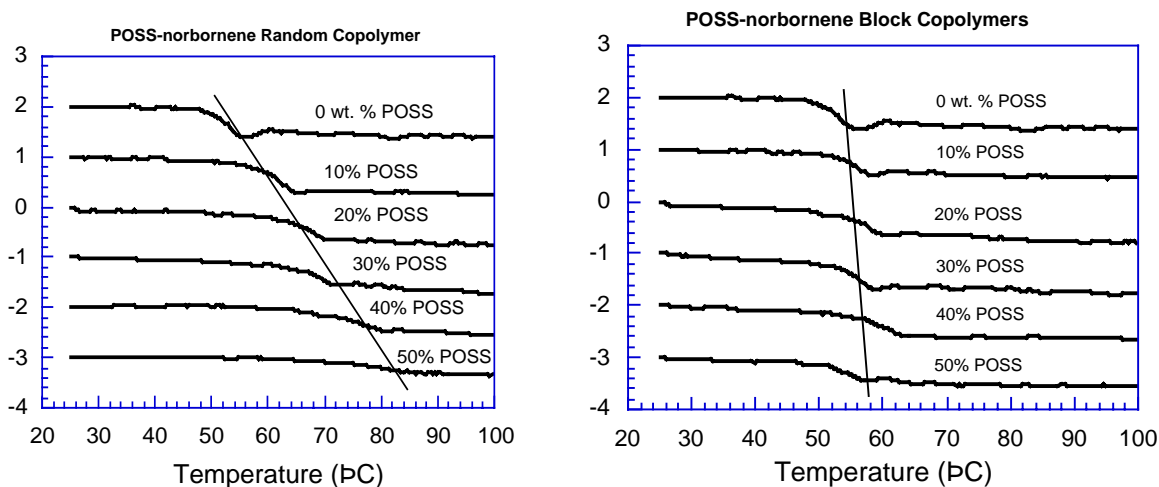
Characterization/property investigations of the POSS-polynorbornylene polymers were undertaken to understand the property enhancement differences for cyclopentyl and cyclohexylPOSS systems by using TEM (collaboration with Dr. Pat Mather while at AFRL/MLBP, now Prof. At U. of Conn.). The TEM's in Figure 4 show the differences in microstructure of the POSS domains within the polymer system. The cyclohexyl system appears to entrain more of the unoriented polynorbornylene chains than the cyclopentyl, which could explain the increase in T_g and increased moduli at both low and high temperatures.
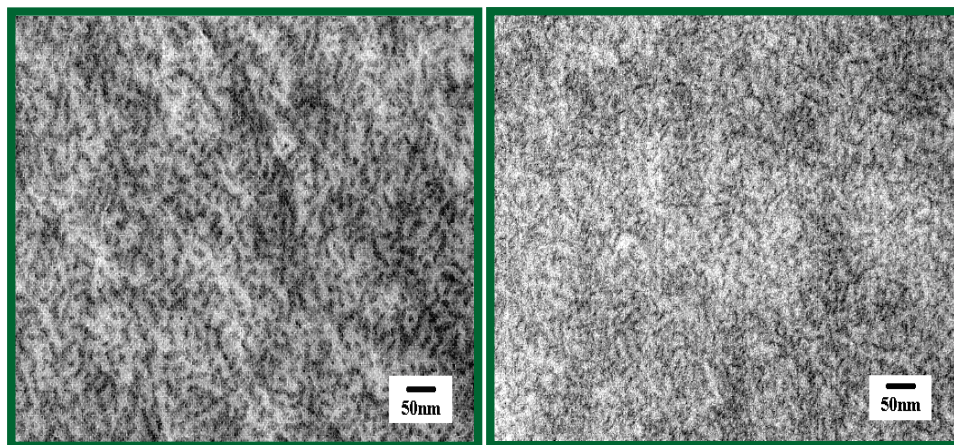

Figure 4   **TEM's of 50 wt. % cyclohexyl (left) and cyclopentyl (right) POSS-polynorbornylene polymers.**

One of the most important things to understand for processing POSS-polynorbornylene polymers, is how the POSS cages interact. A POSS system which is not miscible with the polymer network could agglomerate leading to decreased property enhancements (even leading to failure of the polymer matrix). However, limited agglomeration can lead to strengthening of the material as is observed in POSS containing polymers.

ADHESION TESTING:
Inert propellant was obtained from Jim Harper at NWSC-IH for testing the ability of the POSS-polynorbornylene polymer to adhere to the propellant. (The inert propellant was filled with KCl to simulate the density and morphology of the live propellant, however this resulted in a material with significantly less structural integrity.) The inert propellants (both Hytrel-based and poly-BAMO/AMMO based propellants) were compression molded between two discs of POSS-polynorbornylene polymer at 95 °C and 1000 psi for 5 minutes. The sample were removed and glued to two metal tensile plates. The sample were then placed on a tensile tester and pulled apart at various rates. These tests resulted in failure of the inert propellant, not along the bond line between propellant and inhibitor (Figure 5). This proved that the POSS-polynorbornylene polymer adheres well to the inert propellant and is a good candidate for scale-up and implementation.

Figure 5 **Picture of sample used in tensile tester (Hytrel-type inert propellant plus POSS-polynorbornylene). The POSS sections were glued onto the plates, and pulled apart resulting in inert propellant failure.**

The surfaces of a fractured POSS-polynorbornylene tensile sample and a fractured polynorbornylene tensile sample were compared in a microphotograph. The POSS-polynorbornylene surface shows fibrillar structure (possible indicative of viscous flow during crack propagation). The polynorbornylene exhibits clean break with no fibrillar structure. The presence of POSS in the molecule creates a very discernible difference in the failure behavior of the material.

PROCESSING (Figure 6):
Samples of the cyclopentylPOSS-polynorbornylene were pelletized and placed in a microscale (<5 g) twin-screw extruder, but the load on the screws was to high for processing. As with almost all high-performance polymers a plasticizer was required to increasing processibility. Di-n-octylphthalate was chosen since it is the most widely used commercial plasticizer, and is available in large quantities for pennies on the pound. A studied was performed to determine the minimum amount of plasticizer needed to improve processibility. The wt. % plasticizer was varied from 5 to 15 wt. % with 8 wt. % resulting in the lowest amount required in order to obtain a reasonable screw speed.

The polymer was then heat pressed in a 24-ton hydraulic press at 65 °C and 1000 psi for 5 minutes. The polymer sheet was then heated to 35 °C and, as can be seen in Figure 7, was flexible enough to be rolled onto the Poly-AMMO/BAMO inert propellant. In addition, at 35 °C the propellant and inhibitor readily adhere. The overlapped POSS-polynorbornylene was then sealed using chloroform (although toluene, hexanes, thf, or ether can also be used). The samples sheets of POSS inhibitor were then shipped to NSWC-IH for wrapping and ablation testing.

Figure 6   Rolling of a lightly heated POSS-polynorbornylene inhibitor onto a Poly-BAMO/AMMO stick.

SCALE-UP:

Samples of the cyclopentylPOSS-polynorbornylene were pelletized and placed in a microscale (<5 g) twin-screw extruder, but the load on the screws was to high for processing. As with almost all high-performance polymers a plasticizer was required to increasing processibility. Di-n-octylphthalate was chosen since it is the most widely used commercial plasticizer, and is available in large quantities for pennies on the pound. A studied was performed to determine the minimum amount of plasticizer needed to improve processibility. The wt. % plasticizer was varied from 5 to 15 wt. % with 8 wt. % resulting in the lowest amount required in order to obtain a reasonable screw speed.

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Summary

The synthesis and characterization of the polymer proceeded smoothly along with the scale-up process for 100g quantities. During the down-selection to the primary candidate the POSS-polynorbornylene was selected over the POSS-polyurethane because of easier processing and demonstrated reduced flammability. In addition, the cross-linking of the remaining carbon double bonds of the polymer backbone below the decomposition point of the polymer which could aid in forming a structurally sound char (along with the protective ceramic SiO_2 layer) upon propellant firing. The final goals for the new inhibitor were to test its adherence to the propellant and whether it could be extruded. The POSS-polynorbornylene inhibitor adhered to both the Hytrel-based and the poly-BAMO/AMMO-based TPE propellants, requiring only mild heating (35   C) of the inhibitor prior to wrapping around the propellant. Adhesion tests showed failure within the propellant, not along the bond line. In addition, the use of 10 wt% di-n-octylphthalate, a common plasticizer, resulted in a material that can be readily extruded using a traditional twin-screw extruder. Due to the delay in FY00 funding, samples for live firings were not provided to NSWC-IH (Randy Kramer, 301-744-2578) until the beginning of October 2000. Results will likely be included in NSWC-IH's final report.

Conclusions

Overall, the development of the new POSS-nobornylene inhibitor was extremely successful.   A new inhibitor based
On POSS-polynorbornylene was successfully synthesized and shown to adhere readily to the inert propellants with no bond failure upon testing of tensile strength. The new TPE can be readily processed using traditional processing equipment and with a plasticizer can be extruded. While we have shown for Solid Rocket Motor insulation that POSS incorporation decreases the erosion rate, we do not yet know how the knew inhibitor will behave upon propellant firing. However, based on previous work we believe that the inhibitor will improve the ablation characteristics of the inhibitor.

Transition Plan

In FY99 the POSS nanotechnology was successfully transferred to Hybrid Plastics in Fountain Valley, CA. Hybrid Plastics received a multi-million dollar grant to reduce the cost of POSS nanotechnology from \$1,000 to \$5000/lb down to \$10-50/lb, with AFRL as a subcontractor for the effort. In two years they have brought the price of most POSS monomers down to \$100 to \$500 and POSS molecular silicas (completely condensed with no further functionalization) down to \$10-50/lb. The company is currently working on building a 10,000 lb/year facility. The scale-up of the POSSpolynorbornylene polymer was achieved in house. The initial process used a catalyst (Grubbs catalyst, ruthenium based) that was difficult to remove and accelerated oxidation of the final product. A new catalyst system (Shrock's catalyst, molybdenum based) was successfully used and left behind no significant quantities of catalyst after work-up. In addition, the polymer synthesis and purification was successfully scaled up from 1g to 100g. Further scale-up will require a pilot plant or facilities. We plan to explore the use of the propellant as a combined inhibitor/insulator that is readily extruded. We will work with NSWC-IH on any future missile programs.

Recommendations

Based on the promising results of this program over the three years we believe the program should be continued through an add-on program to address the final issues needed to implement as an inhibitor. The ability to extrude the POSS-polymer is an exciting avenue and with current work at AFRL with POSS-polymers for solid rocket motor insulation the possibility of a combined inhibitor/insulator that is readily extruded could have a huge impact on both cost and weight issues for both boost/orbit transfer motors and tactical missiles.   Also, further work on non-flammable plasticizers would be needed since di-n-octylphthalate, the current plasticizer, is flammable. Scale-up of the POSS-polymer is critical for defense applications and a significant effort is already in place to reduce the cost of POSS monomers and polymers. Work would have to be focused on the particular polymer system, and based on the success of Hybrid Plastics the degree of difficulty is only moderate.

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Publications From This Work

"Hybrid Inorganic/Organic Diblock Copolymers.   Nanostructure in Polyhedral Oligomeric Silsesquioxanes Polynorbornenes" by T.S. Haddad, P.T. Mather, H.G. Jeon, S.B. Chun and S.H. Phillips. Presented at the Materials Research Society Spring Meeting in SanFrancisco, April 24-28 1999. To be published in the Materials Research Society, Symposium Proceedings, Volume 628, 2000.

"New Insight into the Structure-Property Relationship of Hybrid (Inorganic.Inorganic) POSS Thermoplastics" by S.H. Phillips, R.L. Blanski, T.S. Haddad, A. Lee, J.D. Lichtenhan, F.J. Feher, P.T. Mather, and B.S. Hsiao. Presented at the Materials Research Society Spring Meeting in SanFrancisco, April 24-28 1999. To be published in the Materials Research Society, Symposium Proceedings, Volume 628, 2000.

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